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MODELING AND MEASUREMENT STUDY- 1978
Second Year Final Report

by

L. Willard Richards
Kevin R. Johnson
Environmental Monitoring & Services Center
Environmental & Energy Systems Division
Rockwell International
Newbury Park, California 91320

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Project Officer
Robert K. Stevens

Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

An instrumented van was used to collect size-segregated aerosol samples and measure sulfur dioxide and ammonia concentrations on the heavily-traveled Ventura Freeway in Los Angeles while a nearby identical van in radio contact sampled upwind. Measurements were made on a few unusually clean days in October 1978 and February 1979 so that the in-roadway sulfate increment (freeway minus upwind background) could be detected. The average in-roadway increments in the fine-particle size range (less than 2.6 um dia) and nuclei mode size range (less than 0.09 um dia), respectively in ug/m^3 are: sulfate, 0.6 and 0.3; bromide, 2.5 and 1.6; and lead, 5.0 and 2.9. The average in-roadway sulfur dioxide increment 12 ppb or 31 ug/m^3, and the average ammonia in the background was 7 ppb. Sulfates from catalyst-equipped vehicles are in the nuclei mode size range, so at least half the observed sulfate increment is due to other types of vehicles (e.g. diesels). The sulfate increments are much smaller than typical Los Angeles background concentration changes due to driving a mile or two, 24 times smaller than the amount required to neutralize the ambient ammonia, and contain between 1 and 2 percent as much sulfur as the sulfur dioxide increment. Sulfuric acid emissions were easily measured behind a new, catalyst-equipped vehicle using fuel with ten times the California average sulfur content. This report was submitted in fulfillment of Contract No. 68-02-2463 by EMSC, Rockwell International, under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1976 to May 1979.

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1.0 INTRODUCTION

In the 1975 model year, vehicle manufacturers began equipping automobile exhaust systems with catalytic converters to comply with the requirements of the Clean Air Act. These devices have the objective of oxidizing hydrocarbons and carbon monoxide to decrease the emissions of these species. During the early tests of catalyst systems, workers at Ford Motor Company (Pierson, Hammerle, and Kummer, 1974) discovered that catalytic converters have the side result of oxidizing some of the sulfur in the fuel to sulfuric acid. Estimates of the urban and in-roadway concentrations of sulfuric acid which might result from these vehicular emissions led to a concern that the concentrations might be high enough to affect human health. Early work on this problem has been reviewed by Bradow and Moran (1975).

To obtain technical information on how to deal with the problems which might arise from these emissions, the Catalyst Research Program was organized within the EPA, and research was undertaken on:

- sulfuric acid emission rates of vehicles and the factors which affect them,

- development of ambient sulfuric acid measurement methods,

- monitoring to determine sulfuric acid levels near roadways, and

- health effects of fine-particle sulfuric acid aerosols.

The Los Angeles Field Modeling and Measurement Study (LAFMMS) was part of that program, and had the objective of determining both the in-roadway concentrations of sulfuric acid due to catalyst equipped vehicles and the commuter exposure which would result from those acid concentrations.

At the time LAFMMS was initiated, the General Motors Sulfate Dispersion Experiment had been completed and the results reported (Cadle, *et al*., 1976, 1977; Stevens, *et al*., 1976; Wilson, *et al*., 1977). This experiment showed that the buildup of pollutants on and near roadways during stagnant meteorological conditions is limited by the turbulence and heat generated by the vehicles. Therefore, the concentration gradient of the emissions in the vicinity of the roadway is great enough that the population primarily at risk is the vehicle occupants. These results encouraged the focusing of attention in LAFMMS on in-roadway measurements.

As soon as catalyst-equipped vehicles began to appear on the market, the EPA began the Los Angeles Catalyst Study (LACS). The major activity of this program was to operate a series of fixed-site monitoring stations along a line perpendicular to the San Diego Freeway near Wilshire Boulevard in Los Angeles. The concentrations of many pollutants were monitored, including sulfate. The contribution of the freeway traffic to these concentrations was determined by taking the difference between values measured on the upwind and downwind sides of the roadway. At the time LAFMMS began, LACS was reporting sulfate concentration differences across the San Diego Freeway during the afternoon of approximately 5 ug/m^3. That estimate was later revised downwards (U.S. EPA, Los Angeles Catalyst Study Symposium, 1977).

The approach and experimental design used in LAFMMS grew out of an assessment of the magnitude of the sulfate problem by Papetti and Horowitz (1975). They combined information from several sources to make this estimate:

- The Los Angeles Regional Transportation Study (LARTS) computer readable file of vehicle trips taken in Los Angeles which were a statistically representative sample of all trips taken in 1976.

- Weather data from Los Angeles International Airport.

- Best estimates of vehicle emission rates based on EPA and other measurements.

- Upper limits on traffic densities on a congested freeway.

- The HIWAY dispersion model.

The result of their estimate was a number of distribution functions giving the frequency of occurrence of various in-roadway sulfate concentrations and commuter exposures. Their work showed that even though dangerous sulfate concentrations due to vehicle emissions could arise, the probability of this occurring was vanishingly small. Furthermore, concentrations that might be exceeded on occasion, say 5 percent or 10 percent of the time, were not large enough to be a clear threat to human health.

One weakness of their work was that experimental data for in-roadway concentrations of sulfates were not available, so they had to be estimated. The models and emission rates on which these estimates were based contained great uncertainties, so that major uncertainties existed in their final estimates. As long as there was concern about the health effects of sulfate emissions from vehicles, there was a clear need for data on in-roadway sulfate concentrations due to vehicles, and it was necessary that the collection of these data be based on a statistical design which would allow their use in the construction of distribution functions describing the exposure of populations to the sulfate emissions. Because of the uncertainties in the accuracy of dispersion models, there was a need for the experimental measurements to be made in a manner which avoids the use of models in the data reduction. This requirement argues against the use of roadside data as the basis for making estimates of in-roadway pollutant concentrations.

1.1 OBJECTIVE

It is the goal of the Los Angeles Field Modeling and Measurement Study to develop and implement procedures to measure concentrations of sulfuric acid and sulfates due to catalyst equipped vehicles in such a way that the exposure of people can be reliably estimated. The population of prime concern is vehicle occupants on heavily traveled arterial highways.

1.2 MAJOR DESIGN CONSIDERATIONS

The following paragraphs list the considerations which dominated the design of the in-roadway sampling program.

1. The results of the General Motors Sulfate Dispersion Experiment show that the highest concentrations occur on the roadways, so that the population at greatest risk is the vehicle occupants. The present study has chosen to focus on that population.

2. Los Angeles has many multilane freeways with very high traffic densities, and California vehicles are equipped with with air pumps and hence have higher sulfuric acid emission rates than do 49 state cars. As a result, it is expected that Los Angeles will lead the nation in exposure to sulfuric acid or sulfate from catalyst equipped vehicles. In addition, an extensive data base describing trips actually taken in the Los Angeles area is available. Therefore, it is planned to conduct this study in Los Angeles.

3. Atmospheric dispersion models for highways have shown reasonable correlation with experimental data for cases where the perpendicular component of the wind velocity is greater than 1 m/sec, but are still not reliable at the low wind velocities under which the highest sulfate exposures are expected to occur. Therefore, at this time, atmospheric dispersion modeling cannot be relied on when making regulatory decisions related to a vehicle sulfate standard. It is necessary to base the decisions on experimental data.

4. Sulfate emission rates from catalyst equipped vehicles are known to be highly variable, both from vehicle-to-vehicle (even within one vehicle model), and for a given vehicle as it goes through various driving modes. In addition, it appears that the sulfate emission rates for a given vehicle change importantly as the vehicle ages. Several design considerations follow from these observations:

    - Sulfate emission rates are variable enough that determining reliable emission factors as a function of vehicle type and driving mode is impossible. At best, emission rates averaged over vehicle populations and test cycles can be obtained.

    - Sulfate emission rates correlate poorly with emission rates for other pollutants, hence the use of surrogates is not reliable.

    - A field program must sample the sulfuric acid or sulfate concentrations produced by actual, in-use vehicles, and must include the range of driving modes and traffic situations which do occur. However, it is possible and desirable to design statistical sampling experiments so that little or no data need be collected during times when and at places where it is possible to predict that the probability is small that significant concentrations of emitted sulfates will occur.

5. The present difficulties of modeling atmospheric dispersion when the dispersion is poor and in making detailed predictions of sulfate emission rates from catalyst equipped vehicles both strongly suggest that any field study should be as model free as possible. The use of data from one or a few fixed sites requires considerable modeling to estimate the in-roadway exposure of a population in a major metropolitan area.

6. Based on the most recent emission rate data available,

it is thought that the exposures high enough to be of interest can be divided into two categories. (The dividing line between these categories is not sharp.)

- High sulfuric acid or sulfate concentrations may occur over extended sections of the roadway when the dispersion conditions are unusually bad. In this situation, many hundreds or even thousands of vehicles contribute to the exposure of a given individual, so exposures should scale in a relatively simple way with the traffic count of catalyst equipped vehicles and the average emission rate of each vehicle.

- Locally high sulfuric acid or sulfate concentrations may occur behind one or a few vehicles that are unusually strong sulfuric acid sources. Individuals may remain in such local, moving, high concentration regions for many minutes, even tens of minutes. These exposures can occur under a more extended variety of meteorological conditions than in the above case, and would scale with the distribution of vehicular sulfate emission rates in a different way.

7. During the course of the second year of the contract, it became clear that sulfate emissions from vehicles were much less of a problem than was originally feared. Information showing this came from the first year of this contract (Richards, et al., 1977, 1980), the work done by Pierson and his co-workers at Ford (1978, 1979), and information developed in the early part of the second year of this work (see Section 4.1.1). This turn of events was discussed by Maugh (1977). These results made it clear that statistically designed sampling would result in the finding that most exposures to sulfates from vehicles were below the limit of detection of the experimental methods, and suggested that the experimental design be modified part way through the second year of the program.

1.3 A COMPARISON OF FIXED-SITE AND IN-ROADWAY MEASUREMENT STRATEGIES

Since the EPA is already conducting a major monitoring program at a fixed site in Los Angeles to determine the impact of catalyst equipped vehicles, it is important to address the question of why additional measurements might be useful. In part, that question is addressed by the following lists of advantages of each measurement strategy. However, the chief reason additional measurements are necessary is that adequate atmospheric dispersion models and sulfate emission rate data do not now exist to use the data from a fixed site to estimate the distribution of exposures people actually are being subjected to in Los Angeles. In addition, it is not reasonable to expect that adequate dispersion models and emission rate data will become available in the next few years.

1.3.1 Advantages of In-Roadway Sampling

1. Data are obtained at the site of the receptor rather than at a nearby site. Therefore, it is not necessary to use an atmospheric dispersion model to transform the data.

2. Models and assumptions are not required to obtain estimates of the distribution functions describing the exposure of the population at risk. This is especially important when dealing with sulfates from catalyst equipped vehicles for which the emission rates are highly variable.

3. The use of statistical, in-roadway sampling eliminates the possibility of bias due to selecting monitoring sites that are not representative. Only in-roadway sampling can explore the full range of vehicle mixes and driving modes which occur in the region of the study.

4. The in-roadway experimental data include the high exposures which result from following one or a few vehicles with unusually high emission rates. This aspect of the exposure which people are now being subjected to cannot be measured at a fixed site.

1.3.2 Advantages of Fixed-Site Sampling

1. The subtraction of background concentrations from the observed concentrations is simpler (when the wind has an appreciable component perpendicular to the roadway).

2. The data are relatively insensitive to fluctuations in the emissions from individual vehicles, and hence are more easily projected to other vehicle mixes or average emission rates.

3. Fixed sites can operate unattended, and the logistics of fixed site sampling is generally simpler.

1.4 MODIFICATION OF THE EXPERIMENTAL DESIGN

During the course of the work described in this report it became clear that the in-roadway sulfate concentrations were small enough that a sampling program which strictly followed the experimental design would, in the great majority of the sampling runs, find increments in the in-roadway sulfate concentrations below the limit of detection. This result was obtained, for example, in the data discussed in Section 4.1.1. There, it was found that the in-roadway sulfate increment was about a factor of three or four times smaller than the variability of the background sulfate concentration over a distance of one or a few miles. This demonstrated that the in-roadway sulfate increment was both unimportant and hard to measure.

Therefore, the experimental design of LAFMMS was changed in July 1978 to one in which the in-roadway sulfate increment could be reliably determined. This required abandoning certain aspects of the statistical design, and resorting to such measures as performing experiments only on exceptionally clean days when the variability of the background sulfate levels would not mask the in-roadway increment. Also, sampling times long compared to most freeway trips in Los Angeles were used. These modifications permitted obtaining good data for the in-roadway sulfate increment, and showing that the increments were small enough to be of little or no concern. Had the concentrations been high enough to be of concern, they could have been measured with the statistically designed sampling procedure, and no modification of that original design would have been necessary.

1.5 SYNOPSIS OF THE FIRST-YEAR RESULTS

This report describes the results from the second year of a two-year program. The results obtained in the first year are summarized below, and are described in more detail by Richards, *et al*., (1980).

In October 1976, a field program was jointly conducted by the following organizations and project leaders:

Caltech, S.K. Friedlander
University of Minnesota, K.T. Whitby
Washington University, E.S. Macias
Environmental Protection Agency, R.K. Stevens
Rockwell International, L.W. Richards

The program was based at Caltech. The University of Minnesota operated a van and Washington University operated an instrumented car near each other on the freeways, and Caltech operated a van at a fixed site upwind from the freeway segment being studies. At intervals, the mobile van and car also made measurements beside the Caltech van at the background site. Instrumentation included several filter samplers, analyzers to determine the full range of the aerosol physical size distribution, continuous instruments for the criteria pollutant gases, meteorological instruments, and several new instruments being evaluated in the field for the first time.

In the first year study, it was found that in-roadway increments of the sulfate concentrations were small enough that the data scattered about zero on all days. It is believed that an in-roadway increment of 2 ug/m^3 would have been reliably detected, so that the actual increments during the time this program was conducted were smaller. It was estimated that somewhat less than 30 percent of the automobiles on the freeways were equipped with catalysts at the time these data measurements were made.

Sulfuric acid was not reliably detected on the freeway in normal traffic on any sampling day, but it is believed that the measures to protect sulfuric acid samples from neutralization by ambient ammonia were not adequate. Ambient ammonia concentrations were much greater than required to neutralize the possible in-roadway concentrations of sulfuric acid on all test days.

Sulfuric acid was detected in one experiment on the last day of the program when the experimental vehicles followed seven other catalyst equipped automobiles on the freeway in the very early morning. The physical aerosol measurements on that day showed that all of the aerosol increment was in the nuclei mode size range. If the entire volume concentration of the nuclei mode aerosol increment were sulfuric acid in equilibrium with the ambient humidity, it is estimated that the observed concentration behind the vehicles was 3 ug/m^3, and it is further estimated that an average emission rate for the vehicles was 7 mg/mi (4.5 mg/km).

Physical aerosol measurements on all runs except the final special experiment showed that the normal freeway traffic contributed to both the nuclei mode and the accumulation mode size ranges. The grand average increment in the in-roadway aerosol volume concentration was 9.8 um^3/cm^3 in the nuclei mode, with a geometric mean diameter by volume of 0.029 um and a sigma of 1.7, and an increase of 21 um^3/cm^3 in the accumulation mode, with a geometric mean diameter by volume of 0.19 um and a sigma of 1.9.

Other chemical measurements showed the expected increments in the concentrations of elements such as lead, bromine, and chlorine. Increments in the lead concentration in the nuclei mode particle size range as great was 10 ug/m^3 were observed. Filter samples of particles smaller than 2 um collected in the roadway were always dark colored, but samples of larger particles or samples collected at the background site were nearly invisible on the white filters.

Scatter diagrams show that the data for the increase in the aerosol concentration, and the concentrations for sulfur dioxide and carbon monoxide, do not correlate well with the in-roadway concentration of nitrogen oxides. These data demonstrate the problems which can occur if pollutants whose concentrations are known are used as surrogates to estimate the in-roadway concentrations of other pollutants.

As a parallel activity in the first year of the project, a statistically designed sampling strategy and data reduction procedure were developed to determine the exposure of an urban population to high concentrations of pollutants from vehicle exhausts. The mathematical basis of the statistical design is given in a companion report (Fertig, Mann, and Richards, 1979). It is a key feature of the design that distribution functions describing the exposure of the urban population to elevated concentrations of pollutants from vehicles are obtained directly from experimental data without the use of models nor the need to make assumptions regarding the mathematical form of the distribution functions. The distribution functions provide an estimate for each exposure level, c, of the probability that a trip randomly selected from the total population of trips will lead to an exposure of c or more. Conversely, the distribution functions can be used to estimate the exposure level corresponding to prespecified probability of occurrence. The mathematical development includes methods for estimating the variance associated with the distribution functions.

The statistical sampling design is made possible by the existence of a data base representing trips actually taken in the Los Angeles metropolitan area. This was assembled by the Los Angeles Regional Transportation Study (LARTS), and exists in computer readable form. A crucial element of the in-roadway sampling design is the development of an efficient strategy. LARTS trips are combined into trip sequences, such that each sequence can be followed with little wasted time in one working day. Sequences are then selected at random for sampling, and the biases introduced by the use of sequences removed during the data reduction.

This sampling design was reduced to practice in the second year of LAFMMS, as described in the following section.

2.0 DESIGN OF THE SAMPLING STRATEGY

This chapter describes the design and reduction to practice of a sampling strategy for monitoring pollutants in high-traffic areas. The distribution functions giving the exposure of vehicle occupants to in-roadway pollutants are determined. The statistical basis for this sampling strategy was developed in the first year of the contract, and has been reported separately (Fertig, Mann, and Richards, 1979). In the second year of the contract, the strategy was reduced to practice and used. However, the experiments conducted after July 1978 deviated from this because it became clear that the exposure of vehicle occupants to sulfates from catalyst equipped cars was so small that the greatest part of the distribution functions would be within the experimental error of zero. Since measuring a large number of zeros would not be very useful, the experimental design was shifted to focus on measuring the in-roadway sulfate increments on unusually clean days when they could be detected.

Even though the measurement strategy described in this chapter received little use in this project, it still is an important development. It permits the direct determination of the distribution functions that describe the exposure of a population to pollutants whenever the activities of that population can be simulated. The statistical design also provides for determining the variance (uncertainty) of the experimental distribution functions. In the present case, the key to simulating the activities of the population is the Los Angeles Regional Transportation Study (LARTS) data base, which is described in the following section.

2.1 THE LARTS DATA BASE

The approach developed during this contract for statistically designed sampling to determine population exposures depends on the availability and characteristics of the Los Angeles Regional Transportation Study (LARTS) data base. The properties of this data base are outlined here and more information can be found in the Los Angeles Regional Transportation Study "LARTS Base Year Report" (1971).

The Los Angeles Regional Transportation Study was organized within the California Division of Highways, and functions as the technical study arm of the Transportation Association of

Southern California, which in turn is under the direction of the Southern California Association of Governments, a voluntary association of local governments. In 1976, LARTS conducted a origin-destination study for the 9,000 square mile area that includes all of the counties of Los Angeles, Orange, Ventura, and the western, more populated sections of Riverside and San Bernardino counties. At the time, this area was estimated to contain 3,078,200 occupied housing units and 4,321,700 vehicles. One percent of the houses were statistically selected, and when possible, the occupants, 14 years and older, were interviewed to obtain socioeconomic and travel information. The first interview was on the day ahead of the "travel day" for that household. The information obtained by the interviewer the day after the "travel day" included the following data for all trips made by household members five years old and older:

- Trip origin and destination
- Land use at trip origin and destination
- Mode of travel (auto driver, auto passenger, public bus,
- Commodity carried, and commodity weight, if mode was truck driver
- If mode was public bus passenger, how many transfers were required, total cost of trip, and was a vehicle available for the trip
- Trip purpose (work, shopping, etc.)
- If first trip to work, was it in a car pool
- If first trip to work, was it job 1 or 2
- Time spent walking at trip beginning and end
- First on-ramp and last off-ramp, if freeway was used
- Kind of parking space used (lot paid, street, etc.)
- Number of persons in vehicle.

This resulted in a file of 22,330,666 person trips, of which 15,773,538 were driver trips. Emphasis was given to quality control, both in independently contacting 10 percent of the homes to assess the accuracy of the raw data as well as repeatedly checking the data during processing.

When the data base had been assembled, it was used to predict traffic densities through corridors, where physical routing restrictions limited the routes that drivers could take. These data were compared with actual vehicle counts. Also, cordon lines were set up and drivers interviewed to obtain data for verification. In general, the LARTS data accounted for 70 to 90 percent of the observed traffic in these checks.

For the work reported here, copies of the LARTS magnetic tapes were obtained, and the portions of the data of interest were abstracted and stored in a smaller, more manageable file. For example, only trips which included some freeway travel were considered in this study, so all other trips were eliminated.

At the time this work was being done, LARTS was completing the data processing to update the origin-destination survey to the year 1976. Therefore, future work can be based on later surveys than were used in this work.

2.2 OUTLINE OF SAMPLING STRATEGY AND DATA REDUCTION PROCEDURE

Section 1.2 of the Introduction lists the major design considerations which guided the formulation of the statistical design outlined here. Paramount in those considerations is the fact that available models for the emission and atmospheric dispersion of pollutants on roadways are not very reliable, and it is not likely that they will be greatly improved in the near future. Therefore, the strategy was designed to be as model free as possible. Not only is the strategy free of the use of atmospheric dispersion models, but also it is relatively free of assumptions regarding the mathematical form of the distribution functions which describe the pollutant exposures of the population.

It is the objective of the sampling strategy to determine distribution functions which give an estimate of the probability that a randomly selected trip taken in Los Angeles will lead to a (15 min) average pollutant concentration of c or more. Also, the variance (uncertainty) associated with these distribution functions is to be determined. The theoretical development also shows how to invert the distribution functions to determine the concentrations which correspond to various levels of probability.

The sampling strategy which has been devised is analogous to a Gallup Poll. The existence of the LARTS data base makes it possible to statistically select a small sample of trips from that data base, measure the pollutant concentrations encountered when those trips are re-taken, then use those results to estimate the results that would be obtained if similar measurements were made on all trips that people actually did take. This approach requires random sampling, which could be very inefficient if the sampling vehicles have to travel long distances between the sampling runs.

The sampling strategy was made efficient by constructing trip sequences. These are sequences of trips selected from the LARTS data base in such a way that a sampling vehicle has to wait only a few minutes and travel a few miles between the end of one trip from the LARTS data base and the start of the next trip. Time is allowed for filter changing and similar operations between trips. The required randomization in the sampling strategy is achieved by selecting sequences at random. Some bias is introduced, because not all trips are equally represented in the sequences. However, this bias is accounted for and removed in the data analysis.

The criteria which were used in the construction of the trip sequences are as follows:

- Only a portion of the LARTS data base was used. The trips selected started between 0600 and 1100 hours, included some freeway travel, and originated, ended, or passed through the region of Los Angeles County south of the San Gabriel Mountains and the Santa Susana Mountains.

- Each selected trip in the LARTS data base appears in at least one sequence. The number of times each trip appears is known.

- Each sequence can be driven by one sampling vehicle in one workday, with adequate time between trips for the driver to perform any operations required by the sampling equipment.

A full discussion of how these sequences were constructed appears in the following paragraphs.

Once the experimental results are available, they must be reduced. The data reduction procedure has the purpose of combining the experimental data from the in-roadway sampling program so as to obtain $\hat{F}_z(c)$, which is the function that gives the estimate of probability that a randomly selected trip taken in Los Angeles will lead to a measured 15 min average concentration of catalyst sulfate of c or more. (A similar estimate can be obtained for one-hour averages.) The data reduction procedure used is derived and described in detail in an accompanying report (Fertig, Mann and Richards, 1979). However, the steps to be used to convert the experimental observations into the desired probabilities are simple enough that they are enumerated here.

The first step in the data reduction is to average over any replication, that is, to combine the results when more than one sampler measures the same quantity in one car in one trip. The observed concentrations are next converted into probabilities, and all subsequent calculations are performed with these probabilities. This way of doing things makes it possible to obtain unbiased estimates of the desired probabilities from data for stratified samples without making any assumptions about the mathematical form of the function $F_z(c)$.

When calculating $\hat{F}_z(c)$ as a function of c, it is necessary to determine one point on the curve at a time. The overall calculation proceeds in three parts:

- Assume a value for c.

- Represent the observation for each trip as unity if the maximum 15 min average observed concentration was greater than or equal to c, and zero if it was less than c.

- Calculate a weighted average of all zeros and ones to obtain the value of $\hat{F}_z(c)$.

The calculation of the weighted average proceeds as follows:

- The sampling procedure is biased by including some trips in sequences more often than others, making it more likely that these trips will be taken. This bias is removed by dividing the result (a zero or a one) from each trip by the number of sequences in which the trip appears. The resulting values from a given car on a given day are summed and divided by the sum of the weighted factors.

- Then the results for all cars on a given day sampling in the same stratum are averaged without weighting. This average is calculated for each stratum sampled that day.

- The results from all days in each stratum are averaged without weighting to obtain a result for each stratum.

- The results from all strata are then averaged together with a weighting factor to obtain the value of $\hat{F}_z(c)$ at the assumed value of the average concentration c. The weighting factor for each stratum is the fraction of all trips in the portion of the LARTS data base used in this study which fall in the stratum.

These calculations are described in Equations 3.1, 3.8, and 3.9 in Fertig, Mann, and Richards (1979).

The data reduction procedure also includes calculating the variance of the estimates $F_z(c)$. In addition, the information can be reversed to give estimates of the concentrations that correspond to chosen values of the probability, and again information on the variance of those estimates.

2.3 THE CONSTRUCTION OF TRIP SEQUENCES

The construction of the trip sequences began under the first year of this project, and was completed in the second year. The work during the second year was done by John Wilson and Alan Fabrick of Environmental Research Associates.

The main problem to be overcome in the development of a computer program to construct the sequences was devising an efficient search algorithm so that the computer could find trips that connected to make an optimized sampling sequence, yet to avoid the construction of many identical or nearly identical sequences. The method used to solve this problem was to classify all the trips into a three-dimensional matrix with two space coordinates and one time coordinate. Then search a routine for trips to construct a sequence within the bins of this matrix.

Sectional maps of Los Angeles County were obtained from LARTS and were connected to form one large, mosaic map of the entire LARTS region. This map showed the zones which were used by LARTS to code the start and end locations for each trip. Two grids were laid out on the map: an inner one with 19 bins in one direction and 21 in the other for the central, more heavily traveled region of the LARTS area, and a coarser grid with 14 bins in one direction and 22 in the other for outlying parts of the LARTS region. Each LARTS zone was assigned subscripts corresponding to the matrix bin which most nearly fit the zone.

The trip file for this project included all LARTS trips which contained some freeway driving and had start times between or including 6:00 am and 10:59 am on weekdays, with the origin or destination in the part of Los Angeles County south of the Santa Susanna and San Gabriel Mountains. These trips were abstracted from the full LARTS data file, which was available on magnetic tape. Trips were assigned to bins in the matrix according to the time and location of the start of the trip. For the inner, central grid, 20 min time increments were used, and 40 min time increments were used in the outer grid. The full LARTS data base included 7579 trips which fit the above restrictions and were completely enough documented that they could be used. Another 259 trips fit the criteria, but some important element in their description (such as the freeway off-ramp used) was missing or not decodable.

To make sure that each trip is included in at least one sequence, the sequence builder began with the first trip in the file, and worked through the trips in order. If the trip had already been used in a sequence, it was skipped. Otherwise, a sequence was built around it. This required the ability to build sequences both forward and backwards in time. Building sequences by working backwards in time requires knowing when and where the trips end. To save the storage space and effort of creating a second complete trip file with the trips classified by the time and location of their end, string functions were used. These were collections of subscripts in the bins of trip start times and locations which indicated the storage location of trips which ended in that bin.

Each time a trip was included in a sequence, a counter associated with that trip was increased by one so that a number of times each trip is used in a sequence is known. This information is necessary to unbias the data when they are analyzed. The sequence builder continued backwards in time until no further trips (beginning after 6:00 am) were available, and forwards in time until a trip ending after 10:59 am was included (or no satisfactory trip was available). For the inner grid, it was required that 20 min elapse between the end of one trip and the start of the next, to allow time to change filters in the aerosol samplers, adjust the sampling instruments, and to drive to the location of the start of the next trip. In the first search for connecting trips, only those starting within 40 min of the end of the previous trip were considered in the inner grid. Because this 20 min window might span two time bins, both bins were searched for connecting trips. If more than one satisfactory connecting trip was found, the one which had been previously included in sequences the fewest number of times was selected.

When no satisfactory trip was found in the bins first examined, then a second level search was started. First, the acceptable time interval was extended by 20 min. Then an adjacent bin was selected at random from the eight neighboring bins and these bins examined in counterclockwise order. If still no satisfactory trip was found, the time interval was again extended by 20 min and the search repeated. This time, after the adjacent bins were searched, the ones adjacent to them are also search, again in a counterclockwise order. Beyond this, the acceptable time interval is increased without increasing the acceptable geographical area. The construction of trip sequences ended wwen the start time being searched was before 6:00 am or after 10:59 am. This procedure resulted in the construction of a file of 4098 sequences.

To use this file, as many sequences as desired are selected at random, and the information for the times and routes of each trip decoded. The driving plans for the sampling days are then established. Because the vehicle making the background measurements must travel on more lightly traveled (and hence less efficient) routes, the vehicles alternated between making the background and in-roadway measurements so as to equalize their travel times. The use of radios to keep the activities of the two vehicles coordinated is essential.

The trip sequences constructed for this project are on file and can be used in other programs. However, it might be preferable to reconstruct the trip sequences using the existing software to take advantage of updates which have recently been made in the LARTS data base.

2.4 TEST RUNS AND COMMENTS ON TRIP SEQUENCE USE

Test runs were made on May 16 and 19, 1978 with randomly selected trip sequences to evaluate the practicality of sampling according to this strategy. By this time, it was clear that the in-roadway increments in the sulfate concentration were small compared to the background concentrations, so it was not expected that useful sulfate data would come out of these runs. Therefore, only enough runs were done to test the logistics of this type of sampling.

The equipment and analytical methods used in the two trip sequences are described in Section 3.0, which follows. Radio contact between the two vehicles allowed the coordination of their sampling so that the in-roadway and background samples could be collected as close together as possible in time and in sampling location. The sampling went smoothly, and no problems with this method of sampling were encountered.

No further statistically designed sampling was conducted because the in-roadway data then available (see Section 4.1.1) clearly showed that the sulfate increment was so mall that it could only be detected in experiments optimized for its measurement. Satisfactory data for the sulfate increment on heavily traveled freeways could only be determined with sampling times of about one hour (or two hours with the Micro-Orifice Impactor) and the selection of the cleanest winter days for the sampling. At other times, the sulfate levels are high enough and variable enough in the Los Angeles Basin to mask the in-roadway increment of sulfate caused by vehicle emissions. Therefore, had the statistically designed sampling for sulfate been carried out as originally planned, the data set for the in-roadway sulfate increment would have scattered about zero, and would have served no useful purpose, except to put an upper limit on this in-roadway increment. The experiments which were carried out were optimized for the measurement of the sulfate increment (without regard to the estimation of commuter exposure) as were successful in measuring the magnitude of this increment, as described later in this report.

We believe the concept of statistically designed sampling to determine commuter exposures works well in practice, and that it is the best method for determining the exposure of commuters and other vehicle occupants to pollutants which have an in-roadway concentration measurably above the background. Examples of pollutants whose in-roadway increment in concentration is easily measurable at this time are CO, NO, NO , and particulates. Easily measured species in the particulates include lead, bromine, and perhaps carbon. Continuous records of particulate concentrations can include considerable information on the particle size distribution of these particulates.

3.0 DEVELOPMENT OF MEASUREMENT EQUIPMENT AND METHODS

This chapter describes the apparatus and analytical methods used in this study. Section 3.1 describes the vans and the equipment in them used to make measurements and collect samples while traveling on roadways in and near Los Angeles. Most measurements were based on standard analytical methods, which are described in Section 3.2. The two non-standard measurements were those for ambient sulfuric acid and ammonia, which are described in Sections 3.3 and 3.4, respectively. The final section in this chapter describes the design, evaluation, and use of ammonia denuders to protect sulfuric acid on the collection filter from neutralization by ammonia gas in the sample flow.

3.1 THE MOBILE MONITORING EQUIPMENT

Two mobile monitoring systems were assembled in Ford vans which were part of Rockwell's leased fleet of vehicles. The vans were identically equipped, and the apparatus in each of them is listed in Table 1. Van number one was from the 1977 model year, vehicle identification number E14HHZ30123, and van number two was from the 1974 model year, vehicle identification number E24GHV25057. Except for the flame-photometric sulfur gas analyzers, the equipment in each van remained with that vehicle for the duration of the project.

Table 1. Mobile Monitoring Van Equipment

Sampling Manifold with Exhaust Blower
Lawrence Berkeley Laboratory Automatic Dichotomous Sampler
Cabot Corporation Dichotomous Sampler
Meloy Sulfur Gas Analyzer and Strip Chart Recorder
University of Minnesota Micro-Orifice Impactor
Filter Samplers for Ambient Ammonia
Flowmeters for Gas Flow Calibrations
Sears Roebuck Gasoline Engine Driven Electric Generator
Gasoline Engine Driven Vacuum Pump
Motorola Mobile Radio

The sample air was drawn into each vehicle through a three inch (7.6 cm) outside diameter PVC manifold which extended through the passenger front door window to about 50 cm in front of the van windshield and was 170 cm above the ground. The front end of the manifold was capped, and the air inlet was 24 holes 2.5 cm in diameter in the top, bottom, and side away from the vehicle of the part of the plastic pipe which extended in front of the windshield. This design was selected to minimize pressure variations in the manifold due to variations in vehicle speed, which would cause changes in the flame-photometric detector (FPD) readings. (The FPD zero was satisfactorily independent of speed.) A window on one rear door of the van was replaced with plastic to provide access for the vacuum and electrical lines. The sampling manifold was exhausted through a hole in this window by a 265 CFM free air capacity blower, which maintained a strong flow in the manifold at all times.

Electrical power for the sampling equipment was provided by a gasoline engine driven, 3500 watt portable alternator. To minimize the load on this generator, the vacuum for most filter samplers was provided by a Gast Model 1550 carbon vane vacuum pump driven at 1800 rpm by a 3.5 horsepower gasoline engine. Both engines were on a roof rack on the rear of the van, where the effects of their noise and emissions were minimized. Emissions from the engines could reach the samplers only when there was a tailwind with a greater speed than the forward speed of the vans (which could happen at stoplights or in congested freeway driving). Nearly all sampling was on freely moving freeways, so this situation seldom arose. When it did, the filter samplers were turned off.

Inside the van, the sampling manifold, vacuum manifold, and electrical outlet strip all ran along the right (passenger) side. The instrument racks were also on this side of the vehicle, so that access to the back of some instruments was provided by the side door of the van. A gauge on the vacuum manifold was in view of the driver and the instrument operator, so that any loss or weakening of the vacuum would be immediately apparent. Typical gauge readings were 17 to 18 in Hg of vacuum, which correspond to a pressure of 0.6 bar in the manifold. The electrical power for the sulfur gas analyzer and the Cabot sampler was filtered through a Sola Model 23-22-160 CVS harmonic neutralized transformer.

The first instrument on the sampling manifold was the sulfur gas analyzer, which was equipped with a 37 mm Teflon filter to remove particulates, but no scrubber to remove reduced sulfur compounds. The volume flow rate was high enough in the sampling manifold compared to the 86 cm distance between the sampling inlet and the port for the sulfur gas analyzer that negligible sulfur dioxide would be lost to the manifold walls even if it were removed on every collision. The hydrogen for the flame was stored in a Billings Energy Corporation AHT5 metal hydride containing cylinder. This was recharged with pure hydrogen daily, and care was necessary to keep it fully enough charged to provide adequate hydrogen pressure. However, this was easily done.

The zero of the sulfur gas analyzer was determined at frequent intervals on each day by inserting a Meloy SO_x-4 scrubber (serial number 7J018 and 7J019) in the instrument inlet. Multipoint calibrations with a dilution system and a permeation tube with an NBS traceable calibration were performed during each series of experimental days. The linearized output of the instrument was recorded on a strip chart, and the data read from the chart by hand. For most experiments, the instruments listed in Table 2 were used in each van:

Table 2. Sulfur Gas Analyzers

Van Number	1	2
Van Model Year	1977	1974
FPD Model	SA-185	SA-285
FPD Serial	4D085	6E034
Average Zero Drift	3.2 ppb	1.5 ppb

"Fine particle" filter samples were collected in parallel by a Cabot Model 410 Dichotomous Sampler and by a Lawrence Berkeley Laboratory (LBL) Automatic Dichotomous Sampler. The Cabot sampler uses and ERC dichotomous sampling head with a 50 percent cut diameter of 3.5 um when the total flow is 15.8 lpm and the flow for the fine fraction is 14.0 lpm. The fine particle flow is controlled by a Moore Products Model 63BD constant differential pressure flow controller. The sampling vacuum was obtained from the vacuum manifold. The filters were unbacked Teflon with a nominal 1 um pore size obtained in bulk from W.L. Gore Associates and mounted in Cabot 5 x 5 cm aluminum frames. The connection to the sampling manifold was 170 cm downstream from the inlet holes. The instrument required 50 psig compressed gas for automatic operation, and this was obtained from a cylinder of nitrogen.

The LBL Dichotomous Sampler is a two-stage virtual impactor with a 50 percent cut diameter of 3.5 um at a total flow of 50 lpm and a fine particle flow of 47.5 lpm (Loo, Jaklevic, and Goulding, 1976). Flow control is achieved by sensing the pressure drop at the sample inlet with a diaphragm operated switch which operates a servo motor driven needle valve. It was found that the flow controller responded to changes in atmospheric pressure, and it was estimated that this produced flow variations of about 1 percent during the mobile sampling. The sampling vacuum was obtained from the vacuum manifold. The connection to the sampling manifold was 240 cm from the inlet. The fine particulates were collected on 37 mm Teflon filters with a 1 um nominal pore size manufactured by Gore and mounted in 2 x 2 plastic frames by the Ghia Corporation.

Nuclei mode particulates were collected with a Micro-Orifice Impactor (MOI) designed at the University of Minnesota (Liu and Kuhlmey, 1977). Its sample flow was taken from the sample manifold 282 cm from the inlet. Large particles were removed from this flow by two stages of a MRI Model 1502 cascade impactor with smooth impaction surfaces coated with Apiezon L grease. The 50 percent cut diameters used were 3.8 um and 0.46 um. The MOI was deliberately run at a relatively high flow of 28 lpm to obtain a 50 percent cut diameter of about 0.08 um, according to the calibration of Liu and Kuhlmey (1977). The flow was monitored by measuring the pressure drop across the micro-orifice plate. Because of the high pressure drop associated with this large flow, the Gast Model 1022 vacuum pump was used for this sampler.

No filter was mounted in the MOI. The flow from the MOI passed into a manifold with three solenoid valves, each backed by the same kind of filter as used in the Cabot sampler. This permitted collecting three samples in series without stopping to disassemble the MOI and install new filters.

Ambient ammonia sampling was done by first drawing the sample air flow through an inert Teflon filter to remove the ambient particulates (which may contain ammonium) then through two 47 mm glass fiber filters in series which were impregnated with oxalic acid. To minimize ammonia losses in the sampling system, three filter holders were mounted directly to the sample manifold at distances of 98, 109, and 121 cm from the sample inlet. The holders were connected to the vacuum through solenoid valves and then a rotometer, so that three samples could be collected one-at-a-time in sequence. The sample flow rate was typically 20 lpm. The analytical method for ammonia is described in Section 3.4.

3.2 CONVENTIONAL SAMPLING AND ANALYTICAL METHODS

Many of the measurement methods used in this project were conventional, and therefore need be only briefly described. All flow calibrations were performed with mass flowmeters. When calibrating the flows in the LBL dichotomous sampler, care was taken to avoid causing a pressure drop at the inlet, which would disrupt the flow control built into that instrument. Field checks on the sample flows were performed with float tubes whose calibration had been checked against the calibrated mass flowmeters.

The ion chromatographic procedures were those in standard use the EMSC laboratory, except that some modifications were made to improve the lower limit of detection. The exposed filters were stored in sealed containers until an analytical run was performed. The portion of the Teflon filter to be analyzed was removed from the frame by placing the filter, exposed side up, on three layers of Kimwipes. A hardened steel, 37 mm diameter, circular punch was used to cut a disc from the filter. The disc was floated, exposed surface down, on 10 ml of deionized water in a 50 ml beaker. The beaker was covered with parafilm and extracted ultrasonically for 30 min.

When a second hot extraction was used the filter was transferred to a second 50 ml beaker containing 10 ml of deionized water. The beaker was covered with parafilm and heated for four hours at 60° to 80°C. At the end of this time, the sample was ultrasonically extracted for 30 min.

An automated Dionex Model 10 Ion Chromatograph with 3 x 500 mm anion separator and 6 x 250 anion suppressor was used for analysis. The injection volume was about 0.7 ml. The sensitivity of the conductivity dectector was set at 3 umho/cm full scale, and recorders set at 1.0 V and 0.1 V were used to monitor the output of the detector. The full scale recorder output of the conductivity cell is 1.0 V, so that the full scale response of the recorder set at 0.1 V was 0.3 umho/cm. The normal Dionex anion eluent (0.024 M $NaHCO_3$/0.003 M Na_2CO_3) was used at a flow rate such that system pressure was about 600 psi. To maintain the best sensitivity for these analyses, separator and suppressor columns were dedicated only to analyses in which low concentrations of analytes were expected.

Selected samples were tested for water soluble and water insoluble lead. Soluble lead was determined directly on the aqueous extract used for ion chromatographic analysis. The water insoluble lead left on the filters was solubilized by transferring the filters, after the aqueous extraction, into a beaker containing 9 ml H_2O, 1 ml 10 percent HNO_3 and extracting ultrasonically for 30 min. The amount of lead in each of these extracts was determined by graphite furnace atomic absorption spectrophotometry.

The X-ray fluorescence analyses were performed under the direction of T.G. Dzubay of the EPA at Research Triangle Park. The instrumentation and methods used have been previously described (Jaklevic, Landis, and Goulding, 1976; Dzubay and Rickel, 1978; Stevens, Dzubay, Russwurm, and Rickel, 1978).

3.3 THE LOW TEMPERATURE VOLATILIZATION METHOD FOR SULFURIC ACID

The development of the low-temperature volatilization (LTV) method for sulfuric acid was begun at the Cabot Corporation under an EPA contract. The method was proposed by Richards (1973) in response to a request for a proposal by the EPA. The work under the first Cabot contract produced a prototype instrument which operated automatically and unattended (Mudgett, Richards, and Roehrig, 1974a, 1974b), and the method has been patented (Richards and Mudgett, 1974). The prototype instrument was operated by the EPA during the General Motors Sulfate Dispersion Experiment (Lamothe, Dzubay, and Stevens, 1976; Wilson, et al., 1977), and determined amounts of sulfuric acid in the range between 0.7 and 5.4 ug/m^3. Work on this method continued at the Cabot Corporation under EPA funding until 1978, and resulted in the construction and delivery of several additional sulfuric acid sampling units, some of which were also capable of analyzing the collected sulfuric acid. Work on the LTV method was initiated at the EMSC in 1974 under Rockwell funding, then was continued under support from the Coordinating Research Council (CRC). Work done during the first CRC year has been reported (Richards, Johnson, and Shepard, 1978) and the second year CRC report is in preparation (Richards and Johnson, 1980). The method was used in this project for all attempts at determining the concentration of sulfuric acid in and near heavily traveled roadways.

The LTV method uses a two-step procedure for separating sulfuric acid from the other ambient sulfur-containing compounds. In the first step, the ambient aerosol is collected on a Teflon filter, which does not appreciably collect gaseous compounds. In the second step, the sufluric acid is selectively volatilized and transported to a flame photometric detector (FPD) by a warm, dry, methanol-containing air flow. The analysis conditions are chosen so that negligible amounts of compounds such as ammonium sulfate or ammonium bisulfate are volatilized into the FPD. Because the FPD is highly sensitive, and selective to sulfur-containing compounds, this method provides a sensitive and selective technique for determining ambient sulfuric acid concentrations. It is believed that the most important interferences are the neutralization of sulfuric acid on the filter as a result of the interaction with other ambient particulates, and perhaps the existence in the amosphere of volatile, sulfur-containing compounds whose nature is not yet understood (Richards, Wang, and Harker, 1977; Richards, et al., 1977, 1979). Filter storage and shipping procedures have been devised which permit collecting filter samples of sulfuric acid aerosol far from the analytical instrument, shipping them, and storing them for many weeks without measurable change in the analytical results (Richards, Johnson, and Shepard, 1978).

When the development of this method was begun, it was expected that relatively low volatilization temperatures could be used. Bulk sulfuric acid in equilibrium with commercial dry cylinder air (-75°F = -60°C dew point, which corresponds to less than 3 ppm water vapor) at a temperature of 40°C has a sulfuric acid vapor pressure greater than 1 ppm (Gmitro and Vermeulen, 1974), which is enough to drive the FPD out of its linear range. However, early work showed that the physical absorption of sulfuric acid on surfaces is great enough that quantitative data are not obtained at such low temperatures, and that the best results are obtained at the highest volatilization temperature which does not significantly volatilize ammonium bisulfate.

The apparatus used for the LTV determinations of sulfuric acid is similar to the one described by Mudgett, Richards, and Roehrig (1974b), except that the distance between the collection filter and the FPD flame was greatly shortened. The final apparatus configuration is described in detail in Richards, Johnson, and Shepard (1978). The essential part of the apparatus is the volatilization cavity, which will now be described.

The volatilization cavity, which holds the filter with the sulfuric acid deposit during the LTV analysis, is mounted directly to the bottom of the FPD burner block. The dry, volatilization air entering the cavity passes through a preheater, which is 13 cm by 1/8 in (3.2 mm) OD copper tubing whose temperature can be controlled. The cavity consists of two halves, which can be separated to receive the filter, then clamped together to seal the gas flow system. In general, different temperature control procedures are used on each half of the cavity. The system was designed to minimize the distance between the filter and the FPD flame, which was about 2.5 cm.

Both halves of the volatilization cavity and the air preheater are heated with Hotwatt(R) cartridge heaters. All reported temperatures are those of the metal parts as measured by iron-constantan thermocouples. The best analytical results are obtained when the temperatures are reduced as much as possible before the filter is introduced. Therefore, at the start of the cycle, all heater power on the volatilization system is turned off, and the temperature of the volatilization cavity is determined by the rate of heat flow from the FPD burner block (which is always heated). Typically, the upstream half of the volatilization cavity is at 45° to 50°C and the downstream half is near 60°C at the start of the cycle.

After the filter containing the sample to be analyzed is inserted and the system is closed, the heaters are turned on and the electronic integration of the output signal is begun. The air preheater is heated at a constant rate and rapidly comes to a temperature of 120° to 125°C. The upstream half of the volatilization cavity is also heated at a constant rate, and typically has a final temperature intermediate between that of the air preheater and the downstream half of the volatilization cavity. The downstream half, which is exposed to the sulfuric acid vapors, is heated rapidly at high power until its temperature is about 132°C, then the power is reduced to maintain this temperature.

The apparatus used in this work contains digital electronics to control the automatic operation of the instrument. Since the filters were changed manually, much of this control electronics was not used in this work. However, the electronic control of the solenoid valve in the air flow system and the system to reset the signal integrator were used.

The electronics contains a signal processing system to determine the total amount of sulfuric acid volatilized from the filter. The linear output signal from the FPD gives a continuous record of the rate of sulfuric acid volatilization. The linear output signal is integrated by an operational amplifier. The output of the integrator is passed through a variable gain amplifier, which can be used to adjust the calibration of the signal, and then to a digital panel meter.

At the beginning of the analysis cycle, the sampler filter is clamped in the volatilization cavity with all the heaters off and the temperature less than 65°C. Then the heaters are turned on and the cycle begun. Approximately 18 sec later, the solenoid valve is switched to begin the air flow through the filter. About two minutes into the cycle, the temperature in the downstream half of the volatilization cavity has reached the optimum 132°C and the voltage to the heaters for this half is set with the variable transformer to maintain this temperature.

Integration of the linearized output from the Meloy is begun as soon as the air flow is diverted through the filter, and is continued for exactly 15 minutes. After the 15 min integration, the heaters are turned off to reduce the temperature of the volatilization cavity to about 100°C to facilitate removal of the sample filter. The air flow is diverted to the bypass system and the sample filter is replaced with a clean Teflon filter, the cavity is clamped together, and the flow diverted through the filter. The temperature of the volatilization cavity is set to its maximum value (about 180°C), and the cycle is allowed to continue for eight minutes. This step has the purpose of cleaning out the volatilization cavity and minimizing the influence of each volatilization on the one that follows. After eight minutes, the heaters are turned off, and the volatilization cavity is allowed to cool to at least 65°C, and usually 60°C. The instrument is then ready for a new sample.

In typical operation, the apparatus is preconditioned before operation each day and also is calibrated daily. To precondition the volatilization system, about 1 ug of sulfuric acid aerosol is deposited on a filter and a normal volatilization cycle run. For calibration, three filters with amounts of sulfuric acid near 0.2 ug, 0.5 ug, and 1.00 ug are typically analyzed. If data of unusual importance are being determined, additional calibration filters can be included among the unknown filters.

All integrated signals must be corrected for the background signal. In part, the background arises from the fact that the logarithmic amplifiers in the FPD linearizer circuit cannot be set to zero output for zero sulfur input. Also, the volatilization cavity is not always perfectly clean. It has been found that the linear output signal returns essentially to the baseline at the end of each 15 min volatilization, so the background corrections have been made in this work by reading the linear output signal at this time and calculating the output that would have been obtained during a time interval of 15 min at this (background) signal level.

It was found in the Coordinating Research Council funded work on the LTV method that significantly better analytical results were obtained if a silicone compound is used for the pretreatment of the Teflon filters to improve the release of the sulfuric acid during volatilization. The best results were obtained with DC-410, which is a methyl silicone polymer often used as a high temperature stationary phase in gas chromatography. The greatest improvement is observed with amounts of sulfuric acid near the detection limit. The data suggest that a small amount of sulfuric acid is retained by the filter during the volatilization that is independent of the amount of acid applied, and the primary effect of the methanol in the volatilization air and the silicone filter treatment is to reduce the amount of acid retained.

An essential part of the LTV method for sulfuric acid is that a compatible method has been found for protecting filters from neutralization during storage. Teflon filters containing a fraction of a microgram of sulfuric acid aerosol can be stored for at least a month without measurable loss or neutralization of sulfuric acid if they are enclosed in a container in the presence of oxalic acid vapor. At room temperature, oxalic acid has a vapor pressure corresponding to concentrations of about 250 ppb. This acid vapor neutralizes any basic gases which might enter through cracks in the container. Oxalic acid does not interfere with the LTV analysis, and is not acid enough to convert bisulfates into sulfuric acid. The air in the storage container should be left at ambient humidity. If the air is dried, sulfuric acid becomes volatile and could be lost.

3.4 THE ACID FILTER COLLECTION METHOD FOR AMBIENT AMMONIA

The measurement method for ammonia described in this section is related to procedures used in a number of other laboratories (see, for example, Shendrikar and Lodge, 1975) and was reduced to practice at the EMSC before the start of this project. Gaseous ammonia in the ambient air is determined by drawing an air sample through an acid coated filter, which completely absorbs the ammonia as an ammonium salt. This filter is then returned to the laboratory for ammonium analysis. To prevent ammonium in the ambient particulates from interfering, the air flow is first drawn through a filter which removes essentially all of the particulates in the sample flow, but absorbs only a negligible amount of ammonia. In all work in this project, two acid coated filters were used in series. This allowed a check on the completeness of the trapping of the ammonia on the first acid coated filter, and allowed determining the trapping efficiency if the absorption of ammonia was incomplete.

In this work, Fluoropore filters have been used for the front filter, which removes particulates from the sample flow. This material is known to have a high collection efficiency (Liu and Lee, 1976; Liu and Kuhlmey, 1977), and it is believed that a thin Teflon membrane should absorb less ammonia than other filter materials. Gelman A/E glass fiber filters have also been evaluated as a front filter because of their lower cost, excellent particle collection efficiency, and lower resistance to gas flow.

Glass fiber filters coated with oxalic acid have been used for the collection of the ammonia. Oxalic acid was selected very early in this work, and may not be the most satisfactory acid for this use. Its primary disadvantage is that it has an appreciable vapor pressure. Care must be taken in the preparation of these filters to obtain an ammonium blank that is as low and as reproducible as possible.

Gelman A/E 47 mm diameter filters were used, and any ammonium on them was removed by washing first with HCl and then with distilled water. The filters were dried, and then 0.7 ml of 5 percent by weight oxalic acid in ethanol was added to each filter and the filters were dried again in a vacuum. Finally, the filters were stored in closed containers until they were used, and were returned from the field in similar containers.

The ammonium collected on the oxalic acid coated filters was determined by means of the automated Berthelot procedure with nitroprusside as a catalyst. This is also called the indophenol method for ammonium. Care was taken to calibrate the method with standards containing the same oxalic acid concentration as is obtained from the extraction of the filters. In the sensitive range, the method can determine ammonium concentrations in the extract with a relative standard deviation of 4 percent or less in the range between 0.02 ug/ml and 0.2 ug/ml. An extraction volume of 10 ml is typically used, so amounts of ammonium as small as 0.2 ug/filter can be determined with good precision. Therefore, the detection limit of the ambient measurement method is currently determined by the variability of the ammonium blank reading of the acid coated filters.

A Nucleopore 47 mm diameter filter holder, which can be assembled to hold several filters in series, was used. The front filter was at the first filter support grid, and two acid coated filters were held together at the second filter support grid. A pumping system capable of producing up to 25 or 30 lpm flow was also used.

One of the more difficult parts of reducing this measurement method to practice has been the development of a procedure for coating filters with acid in such a way that the ammonium blank is small and reproducible. With the present procedure, the blank values range between 1 and 2 ug/filter and have a standard deviation between 0.1 and 0.3 ug/filter, depending on the filter batch. Therefore, it is necessary to collect about 1 ug/filter of additional ammonium during ambient sampling to obtain useful data.

Blank filters have been sent to the field along with those used in the sampling, and then returned to the laboratory for analysis. These field blanks do not differ significantly from the laboratory blanks, which are determined immediately after the filters are prepared, so the procedures used for storing and transporting the acid coated filters appear to be adequate.

3.5 THE DEVELOPMENT AND USE OF AMMONIA DENUDERS

The determination of ambient sulfuric acid concentrations by filter collection and low-temperature volatilization requires the use of an ammonia denuder in the sample flow upstream of the filter unless one is sure that all portions of the sample flow are acidic. Near variable sources of sulfuric acid, it is quite possible that the sample flow will, at some times, contain sulfuric acid aerosol, and at other times will contain little or no sulfuric acid. When sulfuric acid is not present, the sample flow may contain ammonia gas, which will neutralize the sulfuric acid already collected. In the Los Angeles area, ammonia concentrations of a few ppb are nearly always found (Doyle, _et al_., 1979; Richards and Johnson, 1980), so any air which is not made acid by local emissions or their oxidation products will very likely contain ammonia. Furthermore, non-catalyst vehicles emit ammonia (Harkins and Nicksic, 1967), which increases the chance of obtaining ammonia in the sample flow during in-roadway measurements. For these reasons, it was necessary to use an ammonia denuder in this project.

Denuders have long been used for collecting ammonia gas (Thomas, 1955), and have been successfully used to rather completely remove sulfur dioxide from sample flows (Huntzicker, Hoffman, and Ling, 1978; Cobourn, Husar, and Husar, 1978; Topol and Jackson, 1977). Therefore, it was thought that the construction of an efficient ammonia denuder would be straightforward. Previous work in this laboratory had confirmed Thomas' finding that ammonia denuders performed as theoretically expected at moderate removal efficiencies, and had hinted that there may be problems building high efficiency ammonia denuders (Richards, Johnson, and Shepard, 1978). However, the construction of highly efficient ammonia denuders turned out to be much more difficult than expected.

The theory of diffusion denuders has been described by a number of authors (Gormley and Kennedy, 1949; Thomas, 1967; Ingham, 1975; Richards, Johnson, and Shepard, 1978), and is equivalent to the theory of the heat transfer problem known as the Graetz Problem (Jakob, 1949; Sellars, Tribus, and Klien, 1956). For laminar flow in a round tube, the efficiency of a diffusion denuder depends only on the parameter

$$\alpha = \frac{\pi D l}{Q}$$

where D is the diffusion coefficient of the gas being removed, l is the combined length of all (identical) flow paths, and Q is the total sample volume flow rate. For this project, it was necessary to have a denuder capable of removing a large enough fraction of the ambient ammonia so that only an insignificant portion of the collected sulfuric acid might be neutralized. For ambient ammonia levels in the 10 ppb range, 15 min sampling times and a fraction of the sulfuric acid neutralized equal to the imprecision of the analytical method, it is necessary to have an ammonia collection efficiency of at least 99.8 percent. For this efficiency, the diffusion denuder theory predicts that the parameter alpha should be equal to or greater than 1.6. This means that for ammonia, with a diffusion coefficient of 0.22 cm^2/sec and the Cabot sampler with a flow rate of 15.8 lpm, the denuder must have a total length of 6.1 m. This can be accomplished by constructing a denuder from 20 parallel, identical, 30.5 cm long tubes.

The first denuders used in this project were constructed of 1 cm OD glass tubing set in a hexagonal array using an epoxy casting compound. The first experiments were done with maleic acid coatings. This acid was selected because it is not hygroscopic (in contrast to phosphorous or sulfuric acids), has a much lower vapor pressure than oxalic acid, and has a satisfactorily small pK of 1.83. Coatings were applied by wetting the inside of the tubes with a saturated solution of maleic acid in acetone, and then evaporating the acetone. Obtaining coatings with a satisfactory appearance was not easy.

This denuder and others described below were evaluated by adding known amounts of sulfuric acid aerosol in the accumulation mode size range to a Teflon filter, then passing ambient air through a glass fiber filter, the ammonia denuder being evaluated, and finally through the filter with the sulfuric acid. The purpose of the glass fiber filter was to remove particulates which may neutralize the sulfuric acid deposit on the filter, and thereby interfere with the determination of the performance of the denuder. At the end of the exposure, the Teflon filter was stored in the presence of oxalic acid vapor until analyzed for sulfuric acid by the low-temperature volatilization method. Some filters were also volatilized at a higher temperature to obtain an estimate of the amount of ammonium sulfate and ammonium bisulfate remaining on the filter at the end of the low-temperature volatilization.

Most of the tests of the ammonia denuders were performed with the equipment installed in the vans, to obtain as valid results as possible. A TSI Model 3075 constant output aerosol generator was used to generate the sulfuric acid aerosol, and it was added to the sample air flow downstream from the denuder and upstream from the filter. Typically, the sulfuric acid aerosol addition continued for 1.5 min, during the start of the run, and then the ambient air sampling was continued for several more minutes.

Data from the evaluation of the maleic acid coated ammonia denuder operated at 15.8 lpm and an alpha parameter of 1.6 are given in Table 3.

Table 3. Evaluation of a Maleic Acid Coated Ammonia Denuder

Sampling Duration (min)	Volatilization at 132°C	Net Integrated Response (mV) Additional Volatilization at 180°C	Total
2	46	23	69
3 to 5	20	41	61
5	24	52	76

The response from volatilization at 132°C is a measure of the sulfuric acid on the filter, and the response at 180°C is a measure of the ammonium sulfate and bisulfate remaining on the filter after the volatilization at 132°C. It is apparent that large fractions of the sulfuric acid are neutralized in a few minutes, so that the tested ammonia denuder is not satifactory.

Further experiments were performed with glass tube denuders coated with inorganic acids, such as sulfuric acid or phosphorous acid. Tubes were coated with sulfuric acid by soaking them in a concentrated solution overnight. Phosphorous acid was melted at about 80°C, poured through the tubes, and allowed to solidify along the walls. The phosphorous acid coatings were generally very good. In evaluating these denuders, ambient air was first drawn through a glass fiber filter to remove particulates, then through the denuder at flow rates near 15.8 lpm, then through a Teflon filter which had been spiked with approximately 1 ug sulfuric acid aerosol. At the same time these measurements were being performed, ambient ammonia was being collected on oxalic acid impregnated filters. With the ambient ammonia concentration known, and the quantity of sulfuric acid neutralized, the collection efficiency of the denuder could be calculated assuming stoichiometric reaction between the ammonia and sulfuric acid. In these calculations, it is assumed that the neutralization product is ammonium bisulfate, so that the reported collection efficiency is an upper limit. The results of these experiments are given in Table 4 and Figure 1. In general, it appears that values of alpha need to be about seven times larger than predicted by theory.

Rather than building denuders with 40 to 50 m of glass tubing, use was made of a ceramic material manufactured as a monolithic support for automobile exhaust system catalyst.

Table 4. Tests of Glass-Tube Ammonia Denuders

Acid Used for Coating	Design Parameter	Ambient Ammonia Concentration (a) (ppb)	Calculated Ammonia Concentration at Denuder Outlet (b) (ppb)	Collection Efficiency (%)
Phosphorous	1.60	4.9	> 1.22	< 75
Phosphorous	5.19	4.9	0.07	98
Phosphorous	5.19	4.9	0.17	97
Sulfuric	5.19	4.9	0.44	91
Sulfuric	5.15	4.9	0.54	90
Sulfuric	1.54	11.3	> 1.17	< 90
Phosphorous	4.76	11.3	1.06	91
Sulfuric	4.96	11.3	> 1.18	< 90
Phosphorous	1.60	10.1	> 1.22	< 88
Phosphorous	4.93	10.1	0.83	92
Phosphorous	4.99	10.1	0.46	95

Notes: (a) Estimated to have a standard deviation of ± 0.6 ppb based on the standard deviation of the blanks and the precision of the colorimetric analysis.

(b) Estimated to have a ± 0.07 ppb standard deviation based on a 15 percent relative standard deviation of the low-temperature volatilization determination of sulfuric acid.

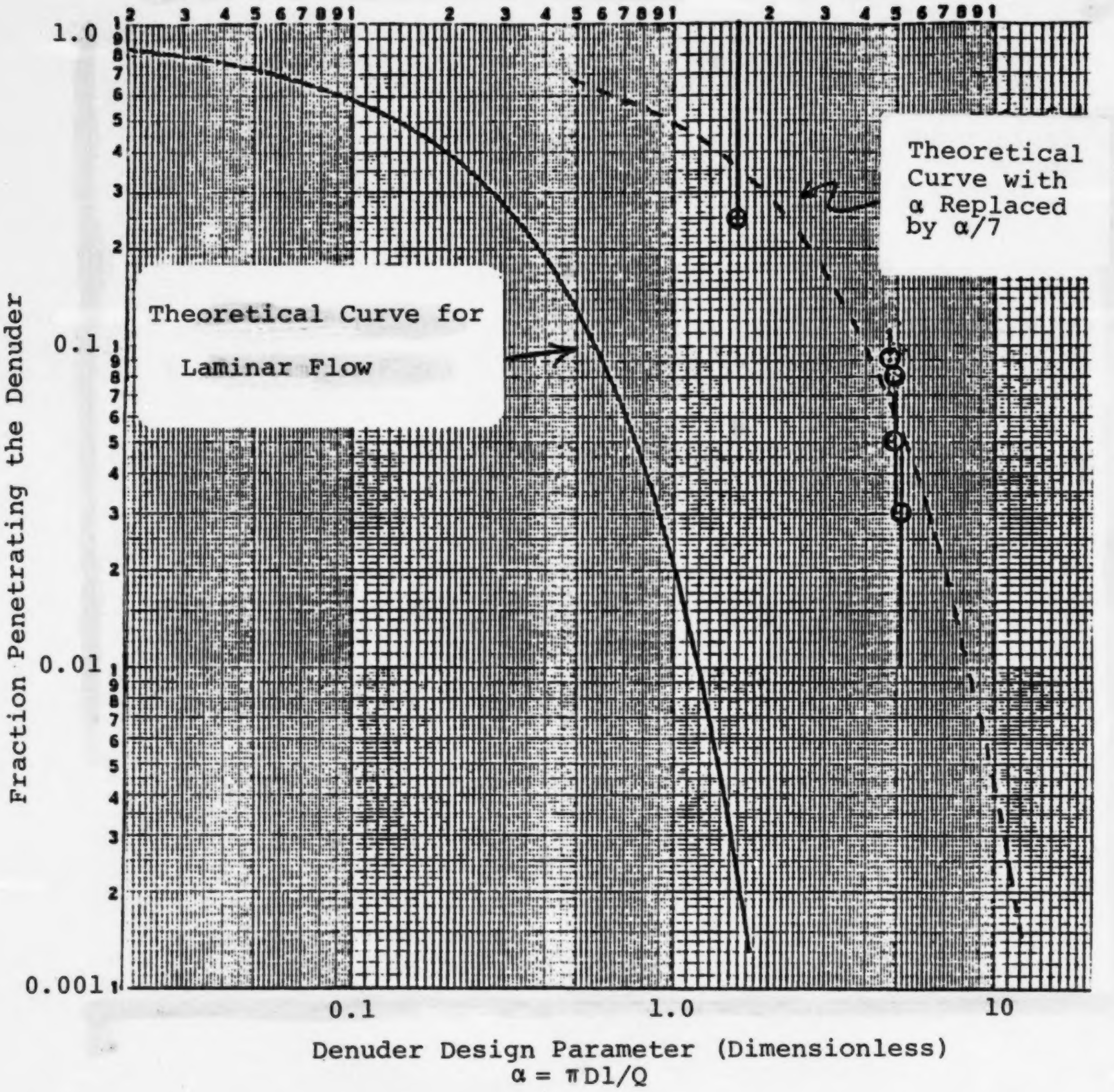


Figure 1. Comparison of the experimental ammonia denuder data with theory for phosphorous acid coatings.

CELCOR, manufactured by Corning, with 300 channels per square inch (47 channels per square centimeter) was used. The denuder elements were 3.8 cm in diameter and 7.6 cm long. The ceramic material itself was porous, and was impregnated by soaking it in concentrated sulfuric acid or molten phorphorous acid. The best performance was obtained from the phosphorous acid impregnated denuders. In three runs, no measurable amounts of sulfuric acid were neutralized behind the denuder. In four out of five runs with sulfuric acid coated denuders, significant losses of sulfuric acid from the filter were observed.

The ceramic denuder coated with phosphorous acid was used for the in-roadway measurements in January 1979 and the chase car experiments conducted in February 1979.

4.0 RESULTS FROM THE IN-ROADWAY EXPERIMENTS

This section contains the results of the measurements made while traveling on congested freeways in Los Angeles. The data are presented in three groups:

- Spring 1978, when the measurement methods were reduced to practice, the feasibility of using trip sequences was demonstrated, and sufficient data were obtained that an error analysis could be performed.

- November 1978, when the experimental design was modified so that good enough data for the in-roadway sulfate increment were obtained, for the first time, to rule out the possibility of zero increment.

- February 1979, when analysis by X-ray fluorescence was included, and the uncertainties in the analytical results were decreased.

These data show that the in-roadway sulfate increment is so small that it can be measured only on very clean days. At other times, it is obscured by the variability in the sulfate concentrations due to other sources in the Los Angeles area.

In all these experiments, sulfuric acid was detected only once, and then was just barely detectable. Its concentration was estimated to be 0.4 ug/m^3. Sulfuric acid was observed in the chase car experiments, so the measurement method is capable of determining sulfuric acid when it is present. On all measurement days, ammonia concentrations were found to be far in excess of those needed to immediately neutralize any sulfate emissions within the roadway.

Good data were obtained for the lead and bromine concentrations in the roadway. As with sulfates, the results from the Micro-Orifice Impactor permitted determining the fraction of these elements which were in the nuclei-mode particle size range.

4.1 SPRING 1978 DATA

The primary purpose of this first set of data was to demonstrate that the measurement methods had been satisfactorily reduced to practice, and that the statistically designed sampling could begin. Samples were collected on a total of 32 different days. In most of the runs reported here, the Cabot and LBL dichotomous samplers were sampling from the same manifold in each of the two vans, so the results are replicated. These data show that the standard deviation of the sulfate concentration difference determination is less than 0.9 ug/m^3. The results include 18 determinations of the in-roadway sulfate increment, and the data from the LBL samplers scatter about a mean of 0.55 ug/m^3, with a standard deviation of 1.68 ug/m^3. Since the standard deviation of the determination is less than 0.9 ug/m^3, the real variability of the atmospheric concentration must have a standard deviation of at least 1.4 ug/m^3 (for this small data set). This variability occurs over the distance between the two vans, which stay as close together as possible and is 3 to 5 times as large as the in-roadway sulfate increment. The fact that the in-roadway sulfate increment is small compared to the atmospheric variability of the ambient sulfate concentration makes it difficult to determine the population exposure to sulfates emitted on the roadway, and clearly shows that there is little need to determine this population exposure accurately at this time.

4.1.1 Sulfate Data and an Analysis of Sources of Variability

The sulfate data obtained through June 1978 from the Cabot and LBL dichotomous samplers are compared in the scatter diagram in Figure 2. The LBL and Cabot fine particle filter samples for each data point were collected in the same van over the same time interval. Therefore, the agreement between these two results is a measure of the precision measurements, including the sample flow calibration and control. It appears that there is a small bias in the flow calibrations in the direction of more sample collected in the LBL sampler, but the five data points above 15 ug/m^3 sulfate concentration are based on ion chromatograph data obtained during the time when their precision was uncertain. Therefore, it is not established that this bias is real. In any case, this bias does not enter into the calculation of the in-roadway increment of sulfate because these differences are always calculated from data from the same type of sampler. Data showing the absence of bias between samplers of the same type are discussed below.

The standard deviation representing the scatter of the data in Figure 2 about the regression lines is 0.5 ug/m^3. All of these results were obtained with a half-hour filter collection time. Figure 3 shows the data in Figure 2 as well as data

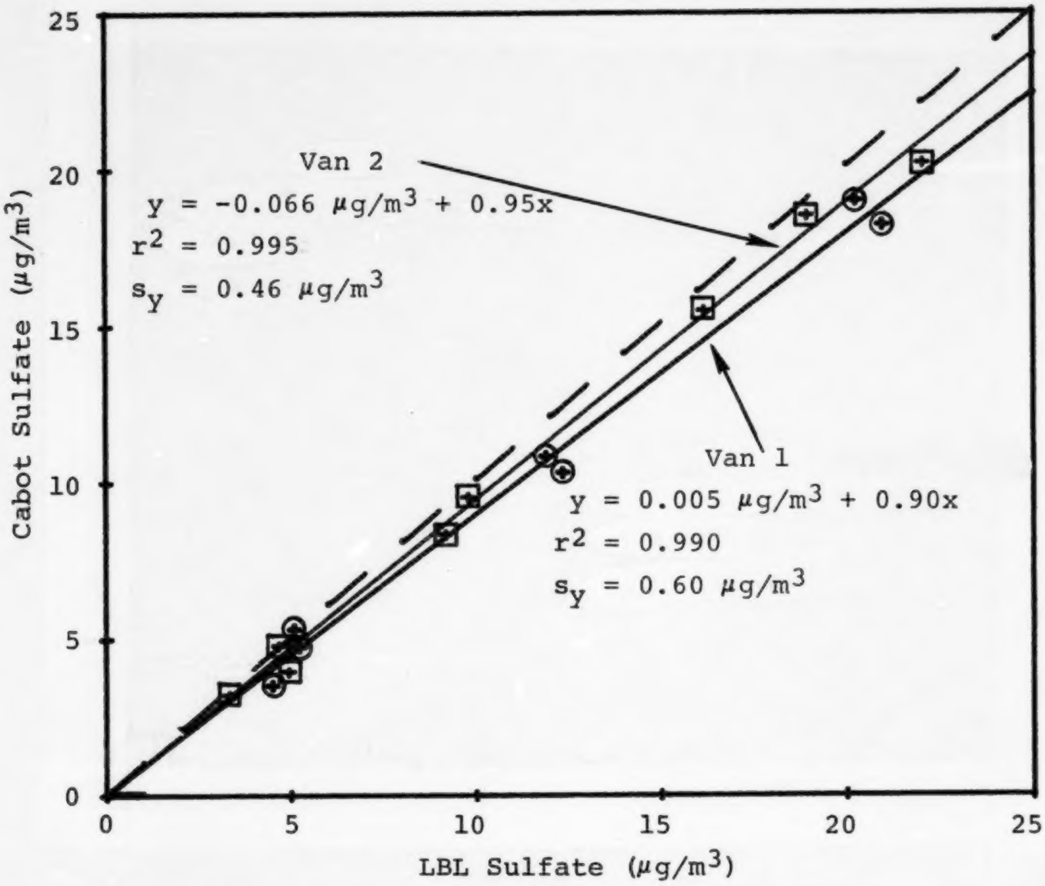


Figure 2. Comparison of LBL and Cabot sampler sulfate data for samples collected on 5, 20, 28 and 30 June only.

⊕ - Van 1

⊞ - Van 2

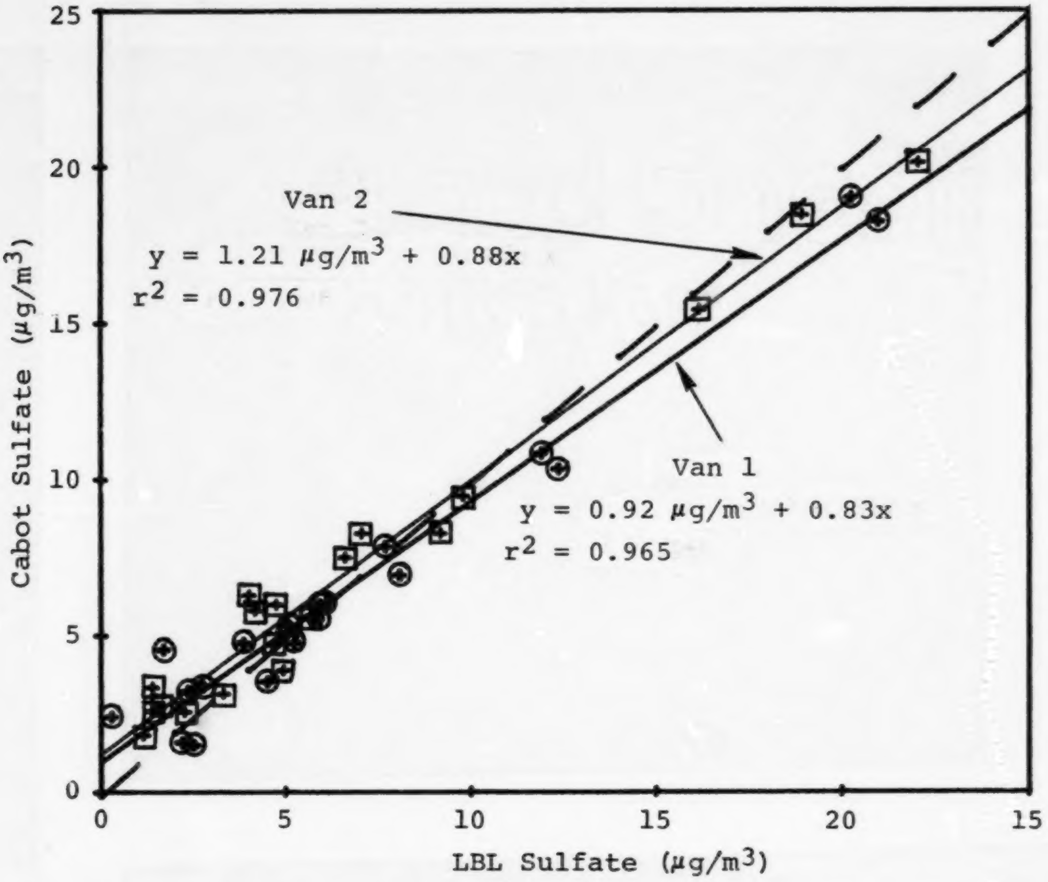


Figure 3. Comparison of LBL and Cabot sulfate data for all samples collected in May and June.

⊕ - Van 1

⊞ - Van 2

collected on May 8, 9, 16, and 19. On the latter two days, 15 min samples were collected on trip sequences selected at random from the trip sequence data base constructed from the LARTS data. On these two days, the standard deviations of the data about the regression lines in Figure 3 are 0.9 ug/m^3 for Unit 1 and 0.7 ug/m^3 for Unit 2. The increased standard deviation was primarily caused by the shorter sampling time, but may be influenced by the problems the ion chromatograph was having at the time these analyses were performed.

All the above data were obtained with the standard 15 to 20 min ultrasonic extraction of the filter at room temperature. To determine the precision of the ion chromatographic analysis of the extract, replicate determinations were made on different days for some extracts. The results are shown in Figure 4, where the absolute difference of the two determinations is plotted as a function of the mean of the two values. The regression line for these data has a slope of 0.02, which corresponds to a difference of 2 percent for large sulfate concentrations. There are few data here for high concentrations. The other data collected earlier on other programs are shown in Figures 5a and 5b. Here the relative standard deviation is 4 percent at the higher concentrations. At low concentrations, the relative standard deviation in Figure 5b rises rapidly with decreasing extract concentration, but the standard deviation itself remains relatively constant at approximately 0.01 ug/ml. All these data are satisfactorily fit by the expression

$$\sigma_x = 0.01 \text{ ug/ml} + 0.03x \qquad (4\text{-}1)$$

where x is the sulfate concentration in the extract and σ_x is the standard deviation of one determination of the extract concentration by the ion chromatograph.

If the ambient data concentration C is calculated from one analysis of a 10 ml extract from a filter which sampled a volume V of air, the standard deviation in C due to the analysis is

$$\sigma_C = 0.1 \text{ ug/V} + 0.03\ C \qquad (4\text{-}2)$$

For 30 min sampling intervals, Equation 4-2 gives the data in Table 5. Here the σ_C for the difference in the standard error of the difference between the ambient concentrations calculated from the Cabot filter and the LBL filter which arises exclusively from the uncertainty of the ion chromatographic analysis of the extract. The data in Figure 2 were obtained in ambient concentrations in the neighborhood of 5 or 10 ug/m^3, and it can be seen that essentially all of the variability of those data can be accounted for by the uncertainty of the determination of the extract concentration. The precision of the flow control in the samplers and the extraction procedure

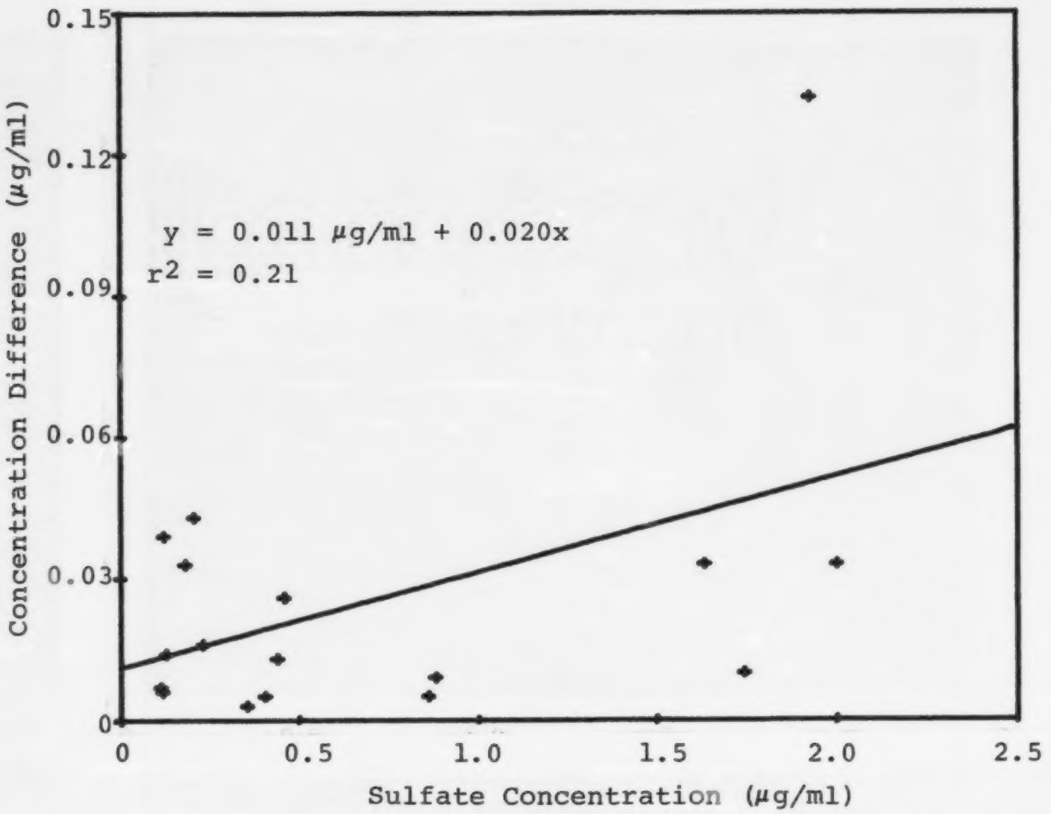


Figure 4. The sulfate concentration difference from replicate analyses of the same filter extract as a function of the sulfate concentration in the extract.

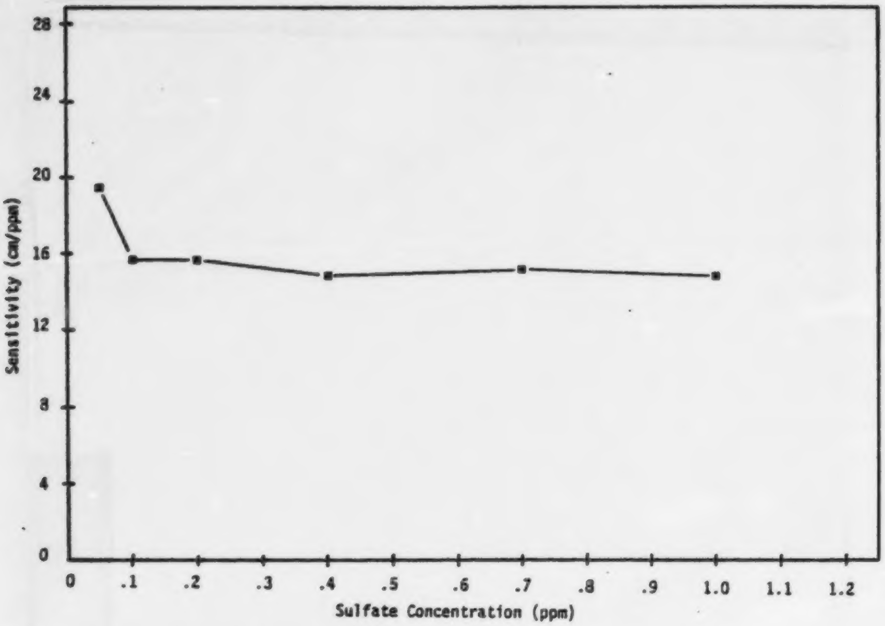


Figure 5a. Sensitivity for aqueous sulfate by Dionex Ion chromatography. Full scale = 1 μmho. (Cheng and Shepard, 1977).

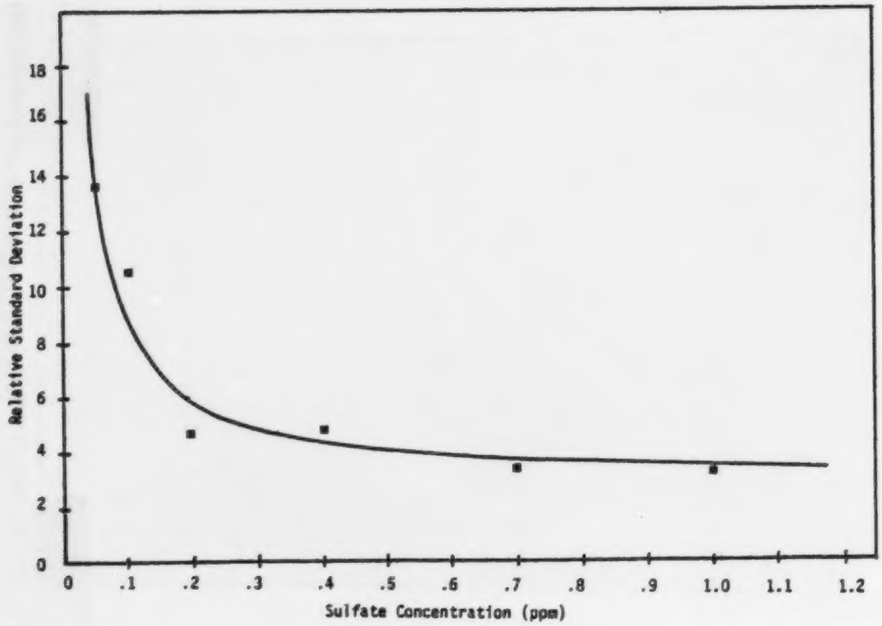


Figure 5b. Precision for the analysis of aqueous sulfate by Dionex Ion Chromatography. Full scale = 1 μmho. (Cheng and Shepard, 1977).

appear to be adequate. As a result, it is expected that replicate analyses of the extract would improve the precision of the results.

Table 5. Standard Errors for 30 Minute Samples
Calculated from Equation 4-2

	Value of σ_3 in ug/m^3 when	
Sampler	C = 5 ug/m^3	C = 10 ug/m^3
Cabot	0.37	0.52
LBL	0.22	0.37
Difference	0.43	0.64

Equation 4-2 explicitly shows the advantage of sampling equipment or strategies which lead to large volumes of air sampled, and Table 5 shows the advantage of the LBL over the Cabot sampler. This advantage is more pronounced for 15 min samples collected at low ambient sulfate concentrations.

In a recent conversation, W. R. Pierson encouraged us to look into the effect of an additional extraction of the filters by heating them at 80°C for four hours followed by another ultrasonic extraction for 30 min. Twenty-three filters were extracted in this way, and data are shown in Table 6, along with the data from the conventional first extration. The sulfate data are also shown in Figure 6. It is apparent that non-negligible amounts of sulfate are obtained in the second, hot extraction. This is especially true for filters which initially contained less than 1 ug of sulfate. Two blank filters have been analyzed to date, and no additional sulfate was recoved from either of them. The Micro-Orifice Impactor data do not appear to differ significantly from the dichotomous sampler data in the fraction of the sulfate which is recovered in the hot extraction.

The fact that additional sulfate can be recovered from the filters by a hot extraction introduces some uncertainty into the data obtained from the room temperature ultrasonic extraction, but this uncertainty is not believed to be great enough to cloud any of the conclusions presented here. The precision of the data in Figure 2 is part of the basis for this belief.

The data for the in-roadway sulfate increment from the dichotomous samplers are summarized in Figure 7 in such way that the agreement between the sulfate difference calculated from the LBL data and the Cabot data can be seen. The great majority of the results fall in the two quadrants which correspond to agreement between data from the two sampling devices. However, the points come close to scattering about zero, which means that the sulfate increment on the roadway is small compared to the

Table 6. Effect of Extraction at 80°C in Obtaining Additional Sulfate, Nitrate, and Bromide. Results are µg/ml extract.

Filter	$SO_4^=$		NO_3^-		Br^-	
	Normal	Hot	Normal	Hot	Normal	Hot
209L	3.79	0.05	0.00	0.00	0.37	na
213M	0.43	0.04	0.05	na	0.03	na
215L	3.77	0.03	0.03	na	0.05	na
218M	0.42	0.06	0.00	na	0.00	na
219M	0.27	(1.77)	0.00	na	0.00	na
224L	3.28	0.05	0.08	na	0.04	na
227M	0.09	0.00	0.02	0.01	0.06	0.02
229M	0.11	0.00	0.02	0.02	0.00	0.02
230M	0.10	0.00	0.01	0.01	0.01	0.00
231blank	0.02	0.00	0.02	0.01	0.01	0.01
232M	0.14	0.14	0.04	0.04	0.08	0.03
238L	0.58	0.07	0.15	0.05	0.04	0.01
239L	0.83	0.02	0.12	0.03	0.26	0.08
240L	0.82	0.03	0.12	0.03	0.34	0.08
241L	0.66	0.03	0.15	0.07	0.02	0.08
244C	0.14	0.00	0.05	0.02	0.01	0.01
265blank	0.02	0.00	0.02	0.02	0.01	0.00
269M	0.10	0.00	0.02	0.00	0.01	0.00
270M	0.11	0.00	0.02	0.02	0.05	0.03
275L	0.88	0.00	0.12	0.04	0.01	0.01
276L	0.86	0.04	0.13	0.03	0.17	0.07
281C	0.18	0.01	0.07	0.05	0.01	0.00
282C	0.15	0.01	0.06	0.05	0.03	0.09

All filters were extracted for 15 to 20 min into 10 ml deionized water in an ultrasonic bath. The results of the analysis of these extracts is listed under the "Normal" column. The filters were then rinsed and then re-extracted into deionized water at 80°C for 4 hours followed by a 30 min ultrasonic extraction. The additional material recoverd with this extraction is listed under the "Hot" column.

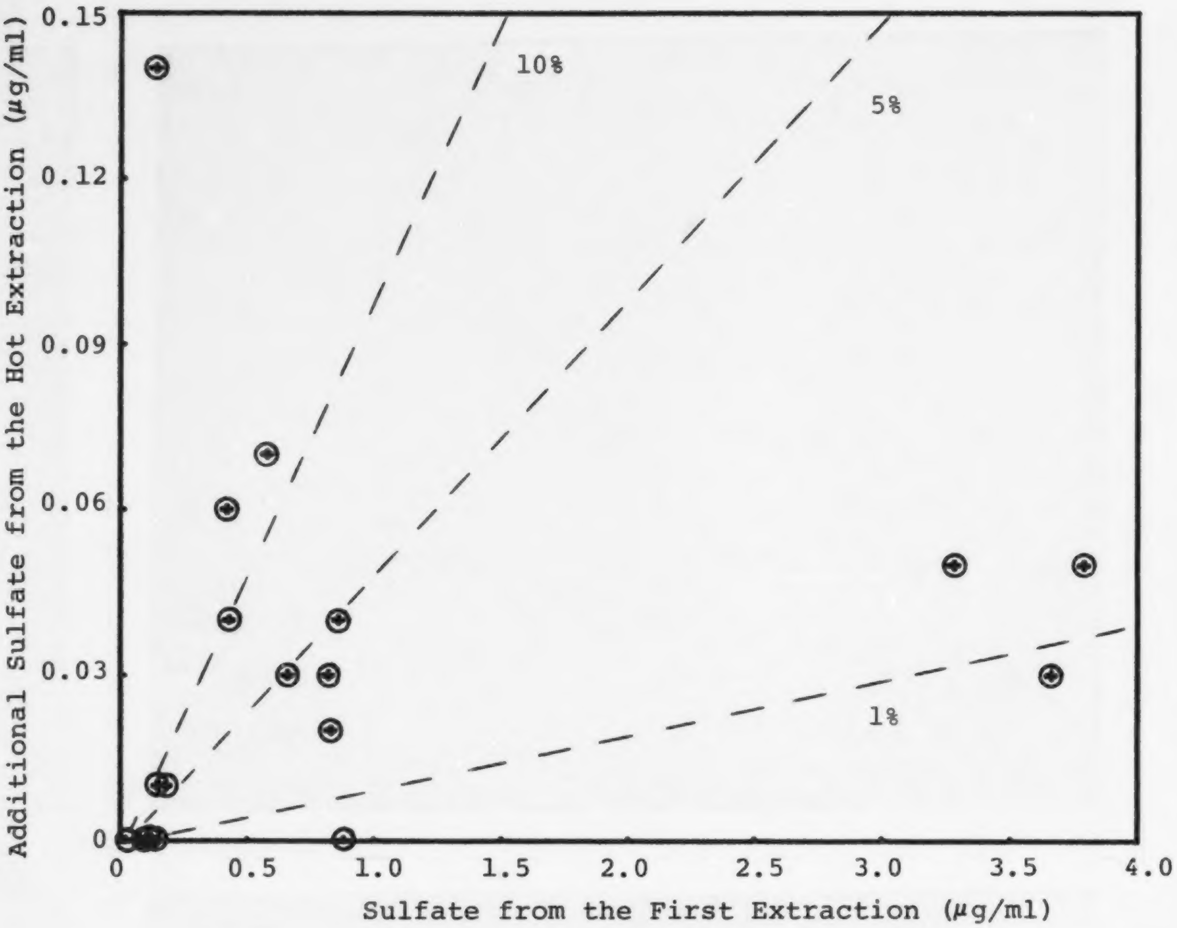


Figure 6. Extract concentrations of sulfate resulting from ultrasonic extraction for 15 to 20 min followed by a separate extraction with hot water followed by 30 min of sonification. Each point represents the data from a single filter. The dotted lines indicate the ratio of the concentrations from the second to the first extractions expressed as a percentage.

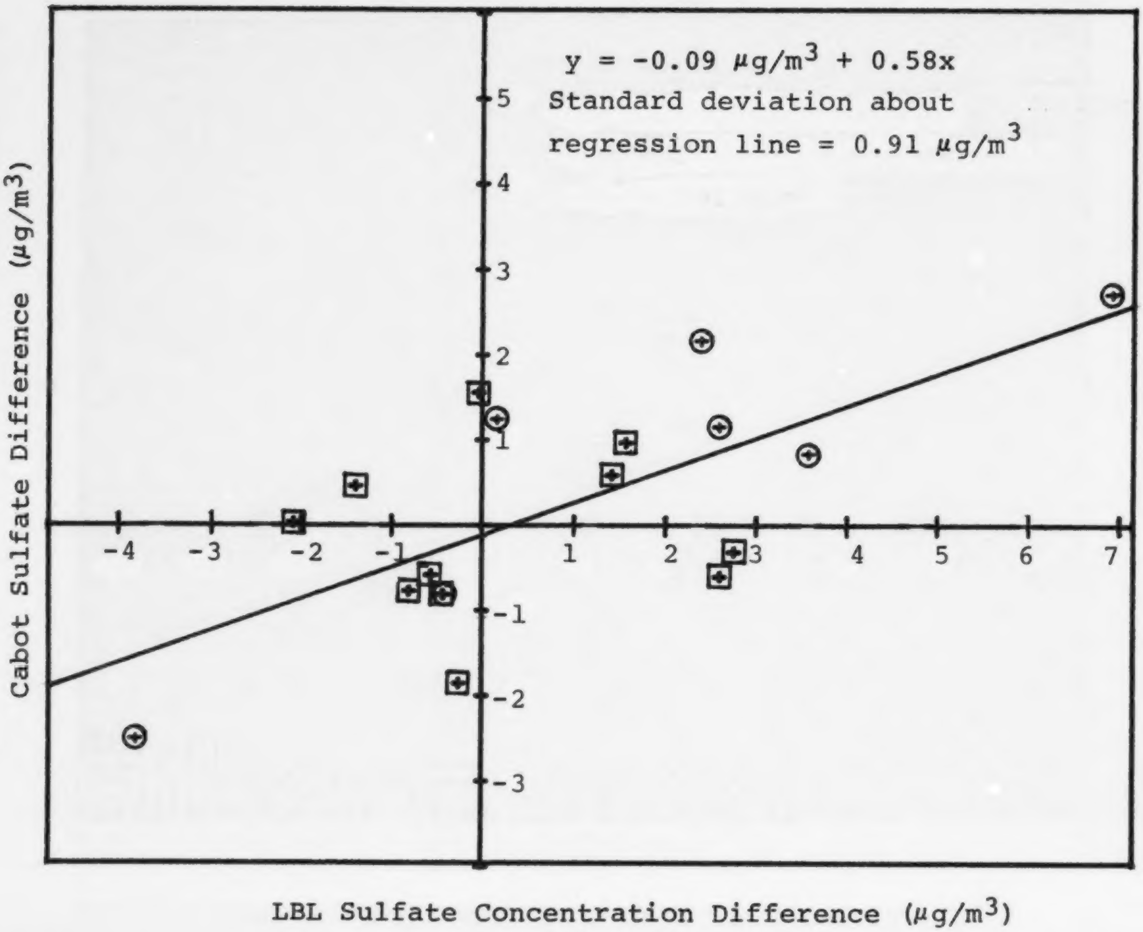


Figure 7. A comparison of the sulfate differences calculated from the data from the Cabot and LBL samplers.

⊞ - Samples collected in May

⊕ - Samples collected in June

precision with which it is determined by the data.

For the LBL data alone, the mean value of the difference is 0.55 ug/m^3 higher sulfate concentration on the road, and the standard deviation of the points about this mean is 1.68 ug/m^3. There are 18 data points, so the standard deviation associated with the mean is 18 times smaller, or 0.40 ug/m^3. Therefore, the mean of the LBL data is not significantly different from zero.

The standard deviation of the data points about the regression line in Figure 7 is 0.91 ug/m^3, which compares favorably with the standard deviation of the same data about the regression line in Figure 3. Therefore, the precision of the differences between data from different types of samplers in the same van is essentially the same as the precision of the differences between data from the same type of samplers in different vans. As a result, it must be concluded that most of the variability in the data for the in-roadway increment of sulfate is due to real variations in the atmospheric sulfate concentration and the necessary separation between the in-roadway and background sampling locations. This separation is typically only a few miles.

The discussion so far has not eliminated the possibility that both the Cabot and LBL samplers in one van contain a flow calibration bias in the same direction. On a few occasions, the two vans have been parked side-by-side with the samplers running, and these data show no bias. Also, the vans alternate taking the roadway and background samples, which eliminates the possibility of bias in the mean value. In addition, no correlation has been found between the sign of the sulfate concentration difference and the van which is collecting the in-roadway sample. Therefore, we believe that if a bias between the vans does exist, it is of negligible magnitude.

The data obtained to date indicate that the roadway increment in the sulfate concentration is smaller than the variability of the ambient sulfate concentration over a distance of a few miles. This can be stated in quantitative terms as follows: The LBL sampler data yield a mean of 0.55 ± 0.40 ug/m^3 and the Cabot sampler data yield a mean of 0.22 ± 0.32 ug/m^3 higher sulfate concentration on the road, where the error is the standard deviation associated with the mean calculated from the scatter of the data about the mean. The standard deviation of the individual LBL sulfate concentration differences about the mean is 1.68 ug/m^3. From the comparison with the Cabot data and the data analysis presented above, we know that the standard deviation associated with the determination of a concentration difference by the LBL is less than 0.9 ug/m^3. Therefore, the standard deviation associated with real variations in the average atmospheric concentration during the sampling time is

$1.68^2 - 0.9^2 = 1.4^2$ or 1.4 ug/m^3. These variations occur over distances as small as can be maintained when one van is operated on a freeway and the other is operated on nearby city streets. Radio contact between the vehicles assured that the sampling times were the same.

This standard deviation of the sulfate concentration difference between two nearby locations of 1.4 ug/m^3 is three to five times the estimate of the in-roadway sulfate increment. Of course, the 1.4 ug/m^3 standard deviation depends on the ambient sulfate concentration, and can be minimized by sampling on days with low sulfate concentrations. However, this spatial variability of the ambient sulfate concentrations in Los Angeles is large enough to make the quantitative determination of the in-roadway sulfate increment quite difficult, if not impossible, during the times of the year when sulfate concentrations in Los Angeles are high.

The Micro-Orifice Impactor (MOI) data have been omitted from the above discussion for two reasons:

A. The data are not replicated in each van, so a similar analysis of the sources of error is not possible, and

B. The MOI data obtained in the spring do not show an in-roadway increment.

These impactors were operated at a flow rate of 28 lpm, which results in a cut size of 0.09 um according to the University of Minnesota calibration (Liu and Kuhlmey, 1978). As a result, most of the accumulation mode sulfate is excluded from the filter sample, and the sulfates from catalyst equipped vehicles should stand out more clearly in the data than the dichotomous sampler data. The fact that the in-roadway increment was not detectable in the Spring 1978 data was a source of puzzlement and concern at the time, but good measurements of sulfate increments in the subsequent fall and winter experiments removed this problem.

A comparison of the MOI sulfate concentration data and data obtained simultaneously by the Cabot and LBL samplers in the same van are shown in Figure 8. The regression lines show that the apparent sulfate concentrations in the nuclei mode size range are 1/5 to 1/6 the concentration in the small particle (nuclei plus accumulation mode) size range. This is the fraction of sulfate that would be expected to be collected if the sulfate were contained in a log-normal distribution of particle sizes with a geometric mean diameter (by volume) of 0.3 um and a sigma of 2.0, which are the parameters typical of ambient aerosols (Whitby, 1978).

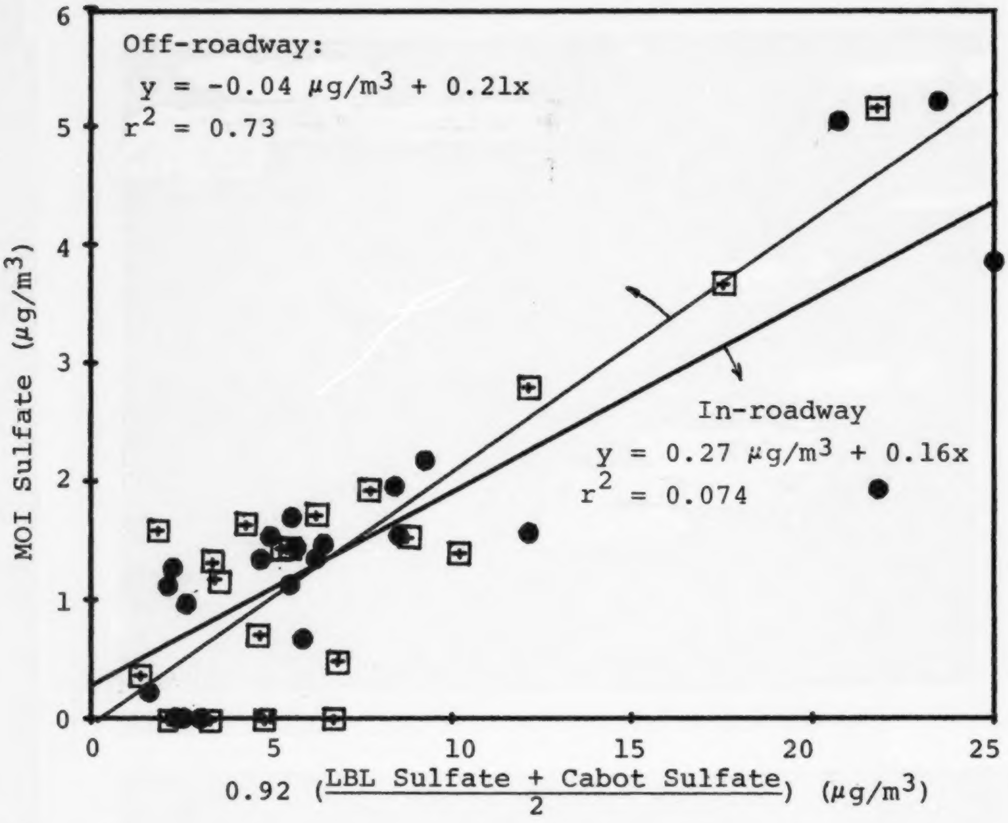


Figure 8. Micro-Orifice Impactor (MOI) sulfate readings compared with the average of the simultaneously obtained Cabot and LBL sulfate readings. The factor 0.92 corrects for an error introduced by the use of incorrect sample flow rates in the original preparation of this graph.

● In-roadway

⊞ Off-roadway

4.1.2 Nitrate and Bromide Data

The ambient nitrate concentrations were below 2 ug/m^3 in most of the data, so the extract concentrations were low enough that the ion chromatographic determinations have a large relative standard deviation. In most cases, the extract concentrations were less than 0.04 ug/ml, which is to be compared with the standard deviation of the analysis, which is 0.01 ug/ml. The data have enough scatter that they are not shown here. The main conclusions to be drawn from them are that the ambient concentrations were usually less than 2 ug/m^3, and that concentrations in this range require the collection of larger sample volumes. Satisfactory nitrate determinations were made in later experiments, and are reported in subsequent sections.

Bromide shows prominently in the ion chromatographs of extracts from filters collected on the roadway. The data in Figure 9 show that the concentrations were appreciably less than the sulfate concentrations, but were determined with satisfactory precision. The bromide concentrations at the background sampling locations were much lower than those found on the roadway.

The Micro-Orifice Impactor data for bromide are of particular interest, because much of the bromide is expected to be in the nuclei mode size range, and therefore, present on the MOI filters collected on the roadway. This is indeed the case. The data from filters collected in June include seven cases on the roadway and seven cases off the road when simultaneous data are available for MOI and LBL samples. The mean values from these data are summarized in Table 7. For sulfate, the MOI/LBL ratio is slightly less than 0.2, so the presence of nuclei mode bromide on the roadway is indicated by these data.

Table 7. Mean Bromide Concentrations

	In-Roadway ug/m^3	Background ug/m^3
Micro-Orifice Impactor	0.84	0.06
LBL Impactor	1.59	0.17
MOI/LBL	0.53	0.37

There are several problems with the bromide data reported here, which make them unreliable, and of qualitative value only. (Good data for bromide are reported in Section 4.3.5.) These problems are:

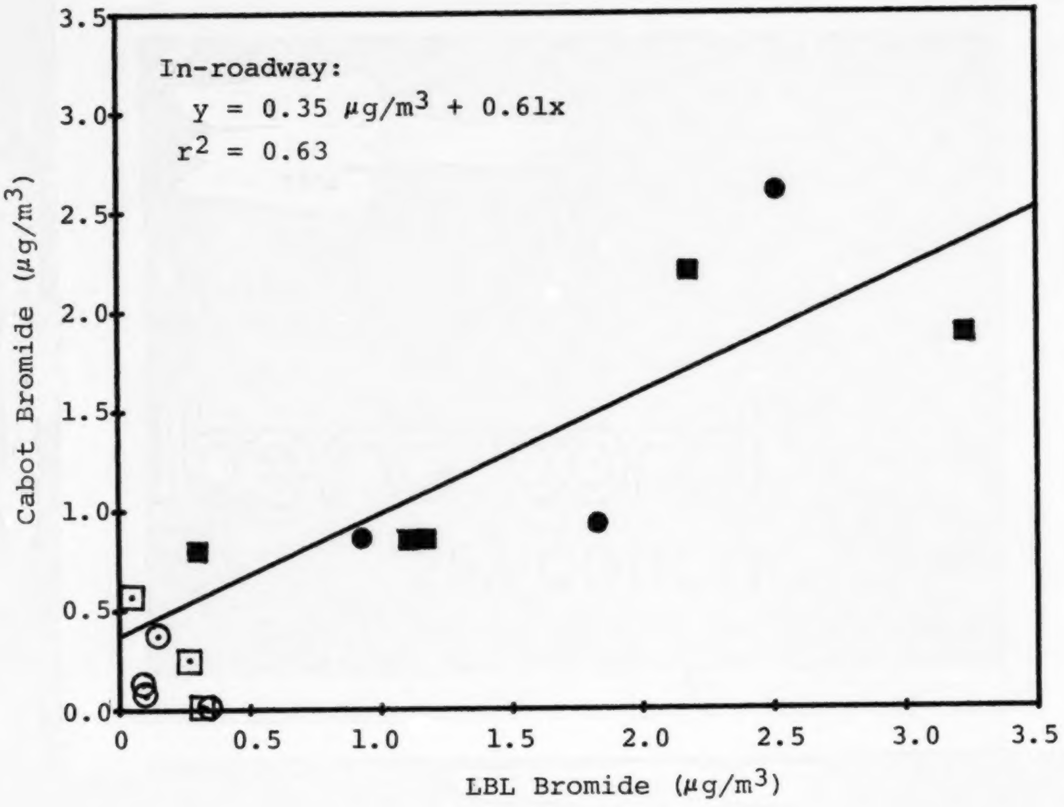


Figure 9. Comparison of the LBL and Cabot sampler bromide data for samples collected in May and June.

	Off-roadway	In-roadway
Van 1 -	⊙	●
Van 2 -	⊡	■

- The data in Table 6 show that significant amounts of bromide are extracted by a second, hot extraction of the filters.

- Background bromide concentrations are low enough to be near the detection limit.

- X-ray fluorescence data in Section 4.3.5 show that incomplete extraction is obtained with the analytical procedure used here.

4.1.3 Discussion of the Sulfuric Acid Measurements

Sulfuric acid has been detected in the roadway on only one occasion. The concentration was small enough to be barely detectable, and was estimated to be 0.14 ug/m^3. This result does not include any correction for the loss of sulfuric acid on the filter due to the interaction with other particulates, which is shown below to be significant.

A series of experiments were performed in the spring of 1978 to quantify the interference in the sulfuric acid determinations which can arise from the interaction of the particulates on the collection filter. Sulfuric acid can be neutralized by these interactions. This interference can be minimized by collecting a small sample. One of the objectives of these experiments was to determine how small the sample had to be to reduce this interference to an acceptable level.

Table 8. Summary of the Data for the Loss of Sulfuric Acid on the Filter Due to Particulate Interactions

Sample Volume per Filter Area (liter/cm^2)	Percent Loss		
	Mean	Standard Deviation	Number of Samples
8-16	53.9	29.9	8
16-24	57.4	32.8	5
24-32	53.5	28.6	8
32-40	59.4	24.6	7
40-48	79.0	15.9	4
56-64	97.0	1.4	2

Table 8 contains a summary of the data from a series of experiments in which filter samples were collected in the roadway or at background locations, returned to the laboratory, spiked with sulfuric acid, then analyzed to determine the fraction of the sulfuric acid which could be recovered and the fraction which was lost. The sulfuric acid analyses were performed by the low-temperature volatilization (LTV) method. In nearly all cases, the amount of sulfuric acid aerosol added to the filter was the same amount as that which would have been collected on the filter if the ambient concentration during sample collection were 2 ug/m^3. The aerosol had a geometric mean particle diameter on a volume basis near 0.1 ug/m^3.

The results are presented in the form of a histogram in Figure 10. It can be seen that the loss of sulfuric acid is significant even for small sample sizes, and does not appear to extrapolate to zero at zero sample size. The standard deviation of the data in each range of sample volume per filter area in Table 8 is rather large, and this is believed to be due to the day-to-day variability of the ambient aerosol concentration. When the data are stratified according to the day of collection, it is found that the day-to-day variation is significant. In particular, the losses of sulfuric acid were less than usual on an especially clean day.

When the data are stratified according to the traffic density, no significant differences are found in the percent loss. This is even true when the background data are included. Therefore, it appears that the ambient aerosol is usually at least as important as the in-roadway emissions in causing losses of sulfuric acid on the collection filter.

On 23 March, experiments were performed in which the collection filter was protected from the ambient particulates by a glass fiber filter mounted upstream in the sample flow. When these collection filters were spiked, no loss of sulfuric acid was observed. Therefore, glass fiber filters remove all of the ambient material which interacts with and destroys the sulfuric acid aerosol on the collection filter.

An estimate of the detection limit for in-roadway sulfuric acid concentrations in these experiments can be obtained as follows. The overall average loss of sulfuric acid in the data in Table 8 is 67 ± 28 percent and the mean sample size is 0.151 m^3. If 0.1 ug of sulfuric acid must remain on the filter to be detected, the limit of detection is

$$(0.1 \text{ ug}/(1.0-0.67))/0.15 \text{ m3}$$

or about 2 ug/m^3.

4.2 OCTOBER 1978 MEASUREMENTS

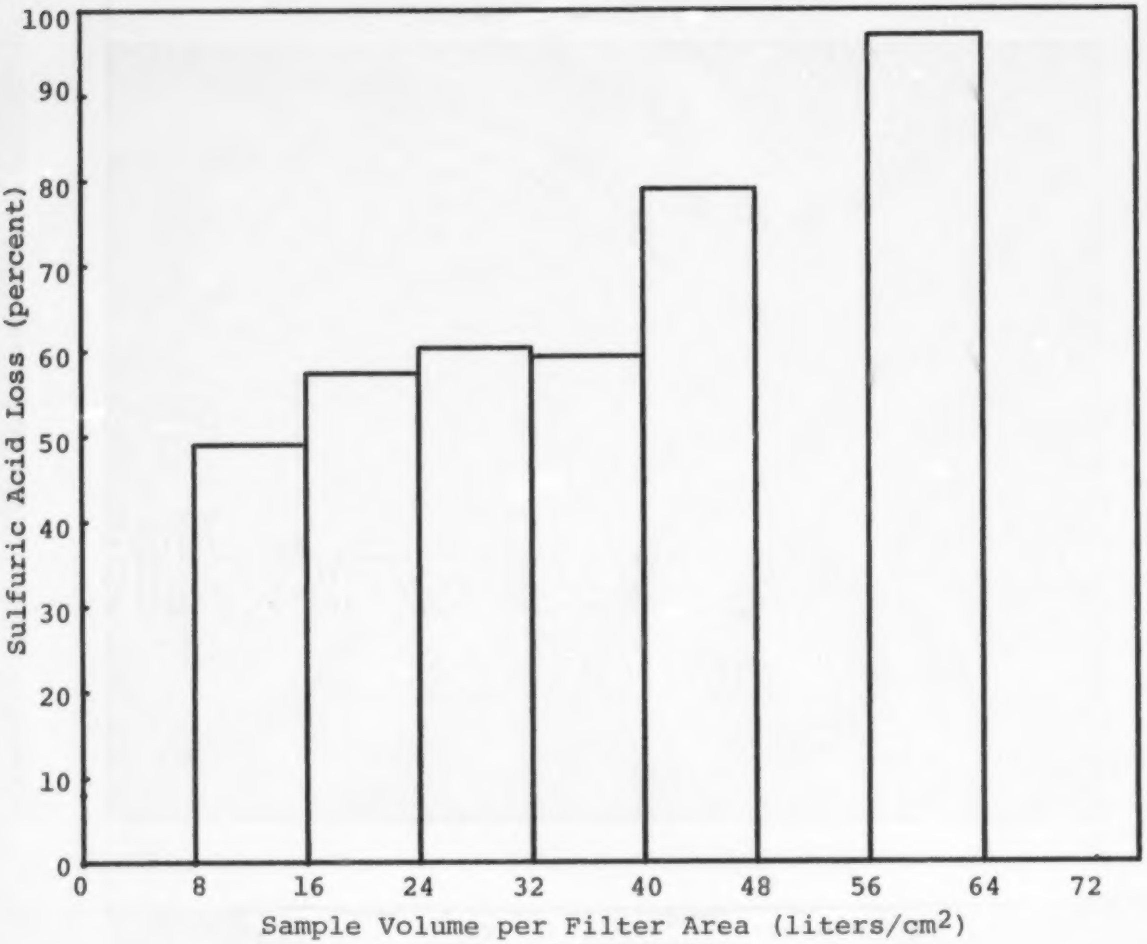


Figure 10. Observed loss of sulfuric acid when sulfuric acid aerosol is added to Teflon filters containing deposits of ambient particulates. In general, the amount of sulfuric acid added was equal to that which would have been collected if the ambient concentration were 2 $\mu g/m^3$.

The sampling strategy for the October 1978 experiments was modified so that the in-roadway increment of sulfate could be measured. The spring data showed that this required one-hour sampling times, and restricting measurements to very clean days. The results obtained in these experiments can be summarized as follows: for the first time, the possibility that the Los Angeles in-roadway sulfate increment is zero is ruled out by the data. The average in-roadway sulfate increment seen by the Cabot samplers was 0.72 ug/m^3 and by the LBL samplers was 0.56 ug/m^3. Sulfur dioxide measurements were also made, and it was found that 0.5 percent to 3.3 percent of the in-roadway increment of sulfur was in the form of sulfate. The observed ammonia concentrations were the same on and off the roadway, and were about 25 times those required to neutralize the in-roadway sulfate increment (assuming all the sulfate is initially sulfuric acid). Excellent precision was seen in the replicate sulfate and bromide data. The atomic absorption lead data showed lower concentrations than expected. Because of the smaller sample size, the Micro-Orifice Impactor (MOI) data are subject to more scatter. On the average, 7 percent of the background sulfate and 38 percent of the in-roadway sulfate increment are in the nuclei mode size range. Also, 29 percent of the background aerosol bromide and 61 percent of the in-roadway particulate bromide increment are in the nuclei mode size range. Nitrate was below the detection limit in the nuclei mode size range.

It is a surprise that the in-roadway sulfate increment does not correlate with the increments of bromide or lead. For very short sampling times, an inverse correlation is to be expected because individual vehicles emit either lead or sulfate, but for the one-hour sampling times used to obtain these data, it was expected that a positive correlation would have been seen.

The experimental measurements were made as follows: simultaneous sampling was performed by two vans on and off the Ventura Freeway in the San Fernando Valley. In any given sample set, one van (with the Cabot and LBL dichotomous samplers, the Micro-Orifice Impactor (MOI), and ammonia filter samplers) operated on the freeway for one hour while the other identical van operated on lightly traveled city streets approximately one mile upwind of the freeway. Two one-hour samples were collected in this way (except that the ammonia sample was collected for two hours), after which the vans traded places and collected two more one-hour samples. The Cabot and LBL dichotmous samplers in each van draw air from the same manifold and collect approximately the same particle size fraction (particles less than 3 um diameter), and this replication allows making an estimate of the uncertainties associated with the sampling and the chemical analysis. The MOI was operated so as to give a 50 percent cut size of 0.09 um. All samples were stored in a refrigerator and analyzed as one batch in November. The sulfur dioxide strip charts were digitized and integrated by computer.

4.2.1 The Sulfate Data

The sulfate concentrations determined with the Cabot sampler are compared with the concentrations determined with the LBL sampler in Figure 11, which shows that they agree well. The standard deviation associated with the determination of the in-roadway increment should be less than 0.7 ug/m^3. The average values for the sulfate measurements are given in Table 9.

Table 9. Average Sulfate Concentrations in ug/m3
Segregated by Sampler for Data Collected in October 1978
(The standard deviation is shown in ().)

	LBL	Cabot	MOI
Total In-roadway	6.37(3.59)	7.23(3.51)	1.02(0.65)
Total Background	5.81(3.74)	6.50(3.36)	0.78(0.82)
Net In-roadway Increment	0.56(0.80)	0.72(1.16)	0.24(0.44)
Number of Observations	9	12	12

The average of the LBL and the Cabot data in Table 9 gives a fine-particle, in-roadway increment of sulfate of 0.64 ug/m^3. The MOI data show that about 0.24 ug/m^3, or about (38 ± 17) percent of this is in the nuclei mode particle size range. The MOI samples were small enough that there is appreciable uncertainty in their values. The 17 percent attached to the 38 percent above is the standard error due to the scatter in the experimental results, and does not include any estimate of systematic errors. Applying the t-test to the in-roadway sulfate increment data indicates that the average is significantly different from zero ($0.99>P(t)>0.95$). These are the first data obtained in Los Angeles which show a statistically significant in-roadway increment in the concentration of sulfate.

Figure 12 compares the total sulfate collected with the MOI to the total sulfate collected with the LBL sampler. There is a significantly higher percentage of sulfate in the nuclei mode on the roadway than off the roadway. This difference in the fraction of sulfate in the nuclei mode on and off the roadway was not seen in the earlier data.

Figures 13 through 15 compare the sulfate differences as determined by the various samplers. For the LBL and Cabot samplers the agreement is as expected; however, the scatter of the data about the regression line is much larger than

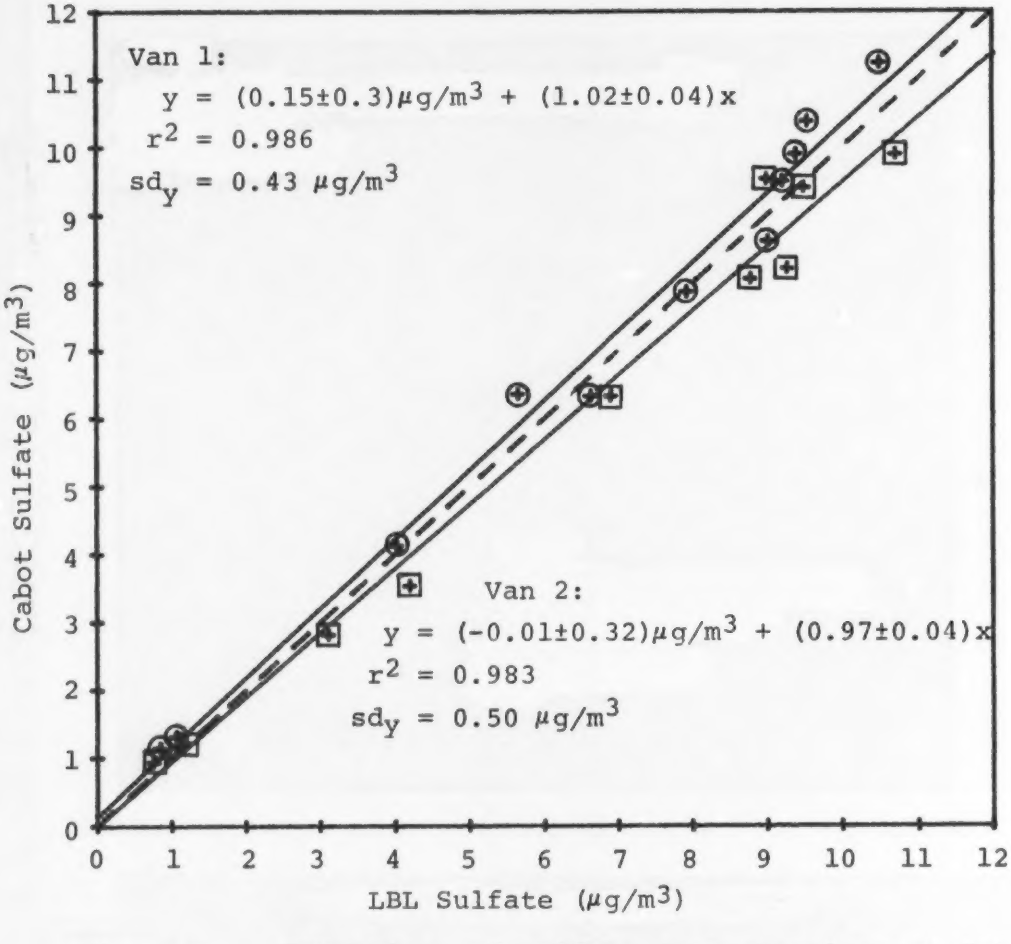


Figure 11. Comparison of sulfate concentrations as determined from filter samples collected in the same van with the Cabot and LBL dichotomous samplers. Samples collected in October 1978.

⊕ = Van 1

⊞ = Van 2

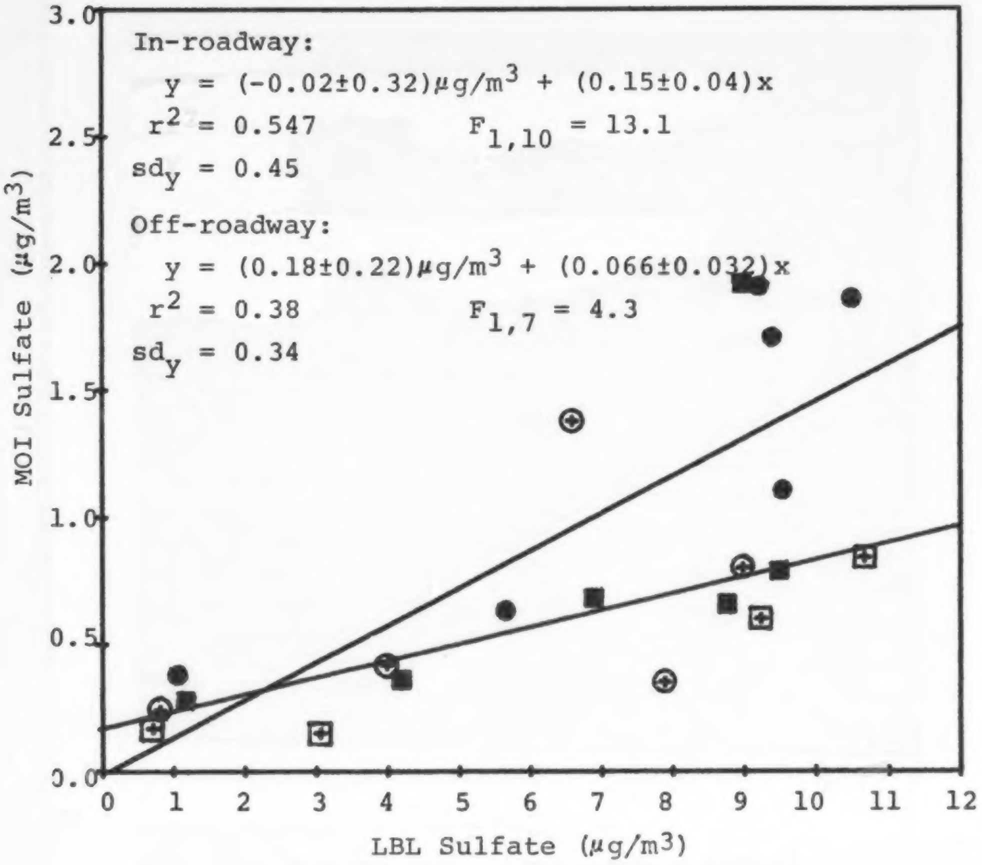


Figure 12. In-roadway and off-roadway Micro-Orifice Impactor vs LBL sulfate. Samples collected October 1978.

	In-roadway	Off-roadway
Van 1	●	⊕
Van 2	■	⊞

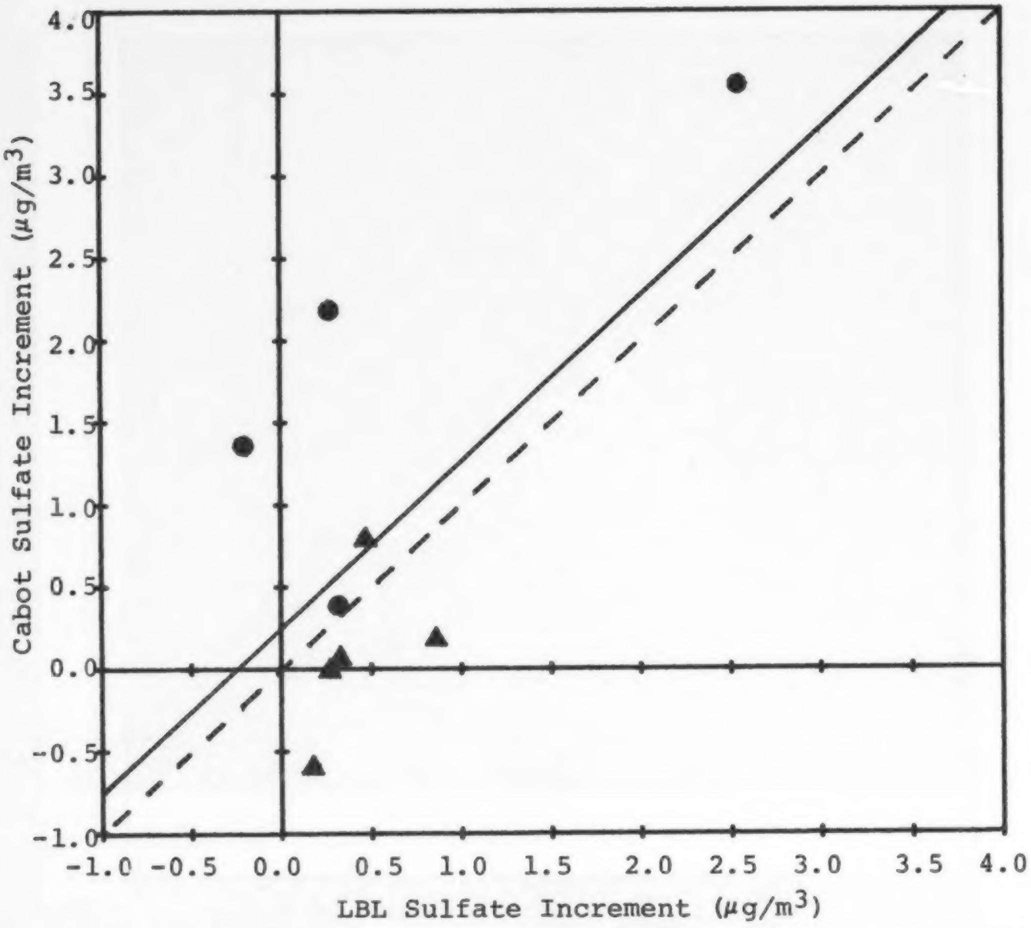


Figure 13. Comparison of the in-roadway sulfate increment as measured with the Cabot and LBL samplers. Samples collected in October 1978.

● Van 1 In-roadway, Van 2 Background

▲ Van 2 In-roadway, Van 1 Background

Regression Line: $y = (0.27 \pm 0.43)\mu g/m^3 + (1.1 \pm 0.5)x$

$r^2 = 0.45$ $F = 5.7$ $sd_y = 1.0\ \mu g/m^3$

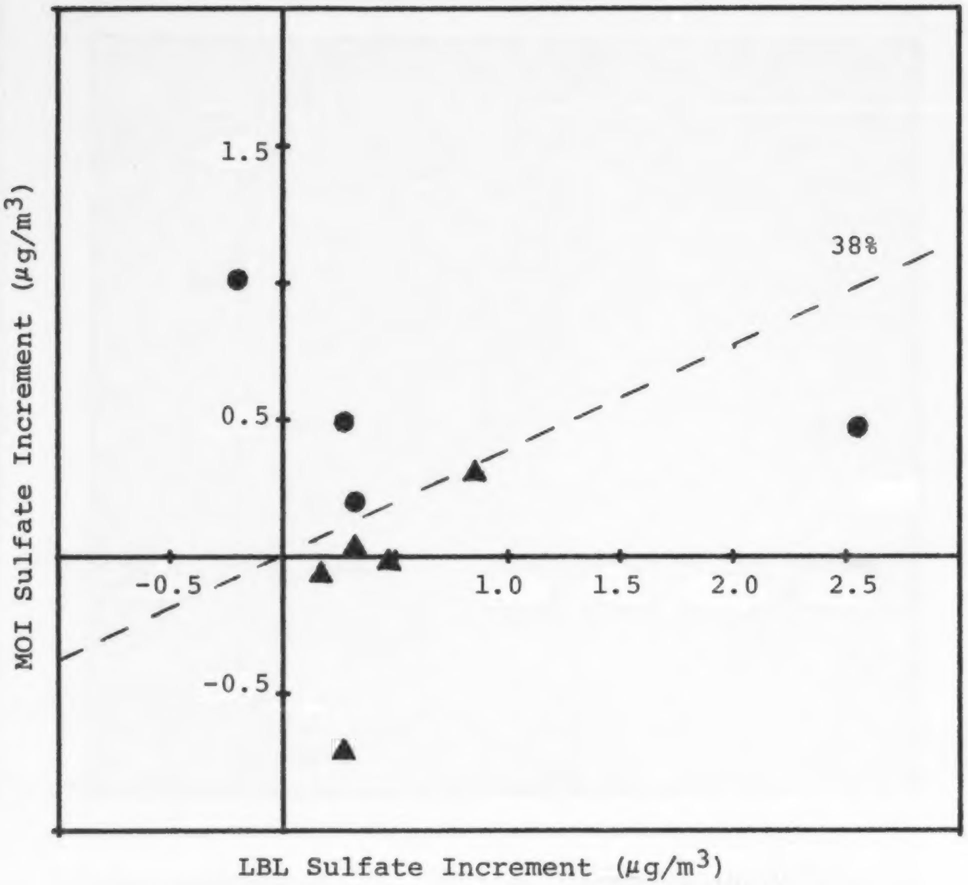


Figure 14. Comparison of sulfate concentration increments as determined from samples collected with the LBL dichotomous sampler and the Micro-Orifice Impactor. Deviation of points about the 38% line is 0.51 $\mu g/m^3$.

● Van 1 In-roadway, Van 2 Background

▲ Van 2 In-roadway, Van 1 Background

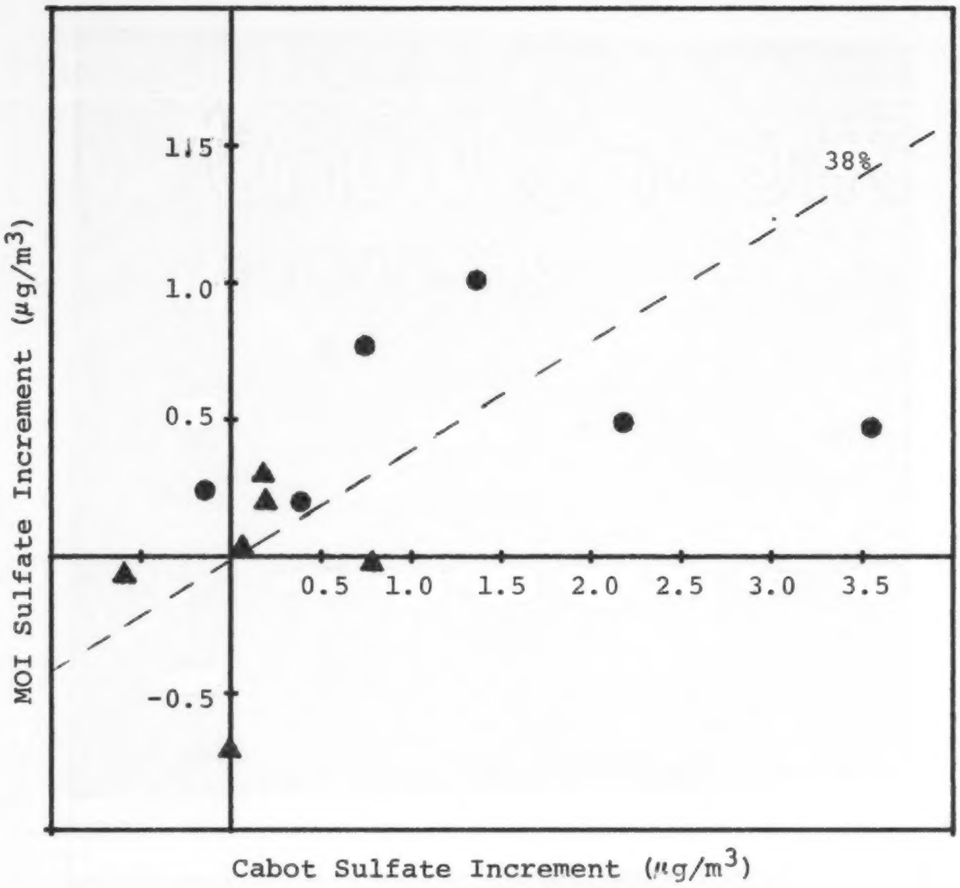


Figure 15. Comparison of sulfate concentration increment as determined with the Cabot dichotomous sampler and the Micro-Orifice Impactor. Deviation about the 38% line is 0.42 $\mu g/m^3$. Samples collected October 1978.

● Van 1 In-roadway, Van 2 Background

▲ Van 2 In-roadway, Van 1 Background

calculated from the variability of the data in Figure 11. As discussed in Section 4.1.1, this additional variability is due to fluctuations in the background sulfate concentrations.

Figures 14 and 15 compare sulfate increments measured by the MOI to increments measured by the LBL and Cabot samplers, respectively. The data show enough scatter that the regression lines were not calculated, but the 38 percent line calculated from the data in Table 9 is shown for comparison.

With the one hour sample times, there was more than sufficient sample on the filters so that the extract concentrations for the Dionex Ion chromatograph were well above the detection limit for filters from the Cabot and LBL samplers. The concentration of the sulfate in the extract from the MOI filters were above the detection limit, but were in a range where the relative standard deviation of the analysis was high. Therefore, the February experiments reported in Section 4.3 were conducted with the one hour sample times for the LBL and Cabot samplers used here, but the sample time for the MOI was increased to two hours.

4.2.2 Nitrate Data

The mean results for nitrate are summarized in Table 10, and the standard deviation about the mean is given in parentheses. Data from the Micro-Orifice Impactor are not included because the extract concentrations were at or below the detection limit of the Dionex ion chromatograph. The values for the in-roadway nitrate increment in Table 10 are not significantly different from zero, which is to be expected.

Table 10. Average Nitrate Concentrations in ug/m3
Segregated by Sampler for Data Collected in October 1978

	LBL	Cabot
Total In-roadway	1.27(1.14)	1.71(1.44)
Total Background	1.28(1.24)	1.65(1.38)
Net In-roadway Increment	-0.01(0.24)	0.06(0.25)
Number of Observations	11	12

Figure 16 gives the comparison of the nitrate concentrations as determined by the LBL and Cabot samplers in the same van. The agreement between the two samplers is much better than that obtained in June and can be attributed to the 60 minute sampling time. At the higher nitrate concentrations

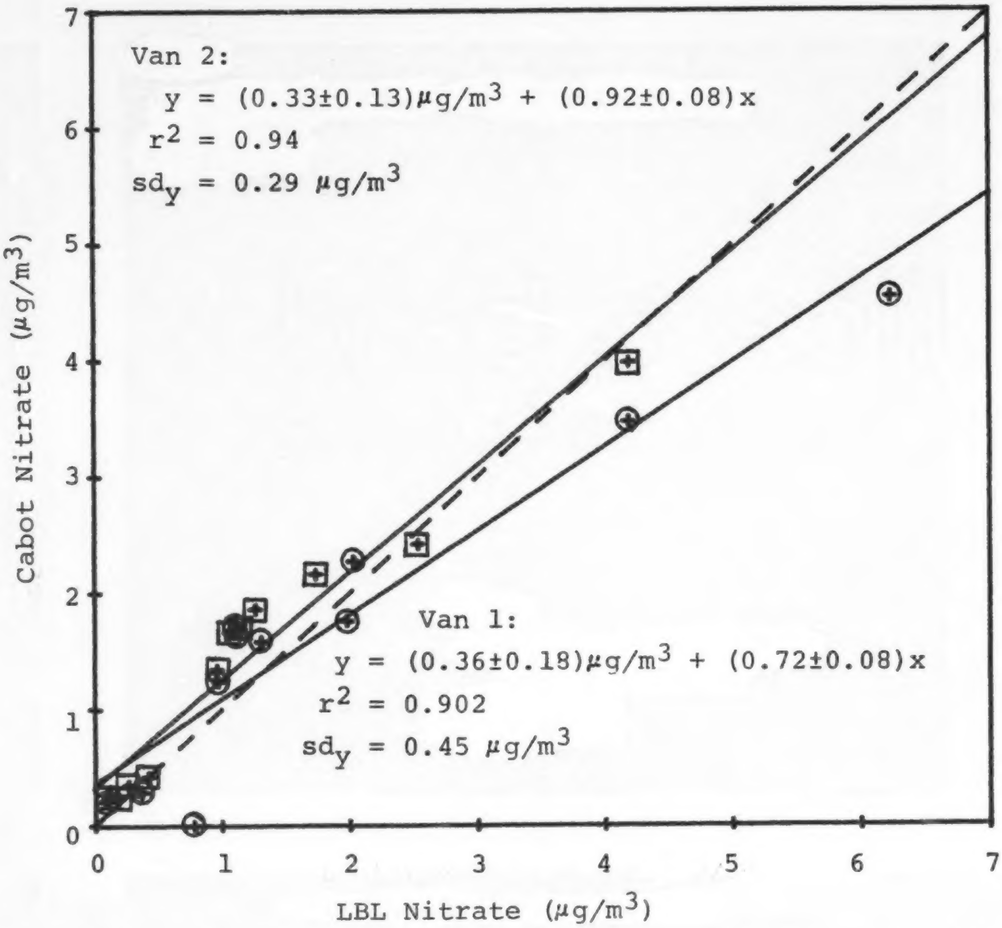


Figure 16. Comparison of nitrate concentrations as determined from filter samples collected with the Cabot and LBL dichotomous samplers in the same van. Samples collected in October 1978.

⊕ - Van 1

⊞ - Van 2

the LBL sampler appears to collect more material per unit volume sampled than does the Cabot sampler. This is not due to flow perturbations because there is no disagreement for the sulfate or bromide data.

Figure 17 is a scatter diagram for the in-roadway increment of nitrate above the background and it shows that the points do scatter around zero.

4.2.3 Bromide Data

The bromide data are presented in Figures 18 through 21 and in Table 11. Of all the species analyzed, bromide gives the most consistent results. This is reflected in the comparisons of the total concentrations and the increment concentrations. In this data set, approximately 61 percent of the emitted bromide is in the nuclei mode on the roadway, and about 90 percent of the roadway bromide concentration is due to vehicle emissions on the roadway being studied and only 10 percent is due to emissions from traffic on other roadways.

Table 11. Average Bromide Concentrations Segregated by Sampler for Samples Collected During October 1978 (ug/m3). (Standard deviation about the mean is shown in ().)

	LBL	Cabot	MOI
Total In-roadway	2.09(0.78)	2.26(0.90)	1.26(0.54)
Total Background	0.28(0.16)	0.30(0.19)	0.08(0.03)
Net In-roadway Increment	1.81(0.79)	1.96(0.92)	1.18(0.52)
Number of Observations	11	11	12

The excellent precision of the bromide data, the agreement between the two dichotomous samplers, and the remarkably small amount of scatter in Figure 21 indicate that the variability in the sulfate and nitrate data is not due to variability in the filter collection, and probably is not due to variability in the filter extractions. It is quite likely that most of the variability in the sulfate data is due to real variability in the atmosphere being sampled.

The bromide data presented here are subject to a difficulty discussed in Section 4.3.5. There a comparison between XRF and ion chromatography data shows that the extraction of bromide is

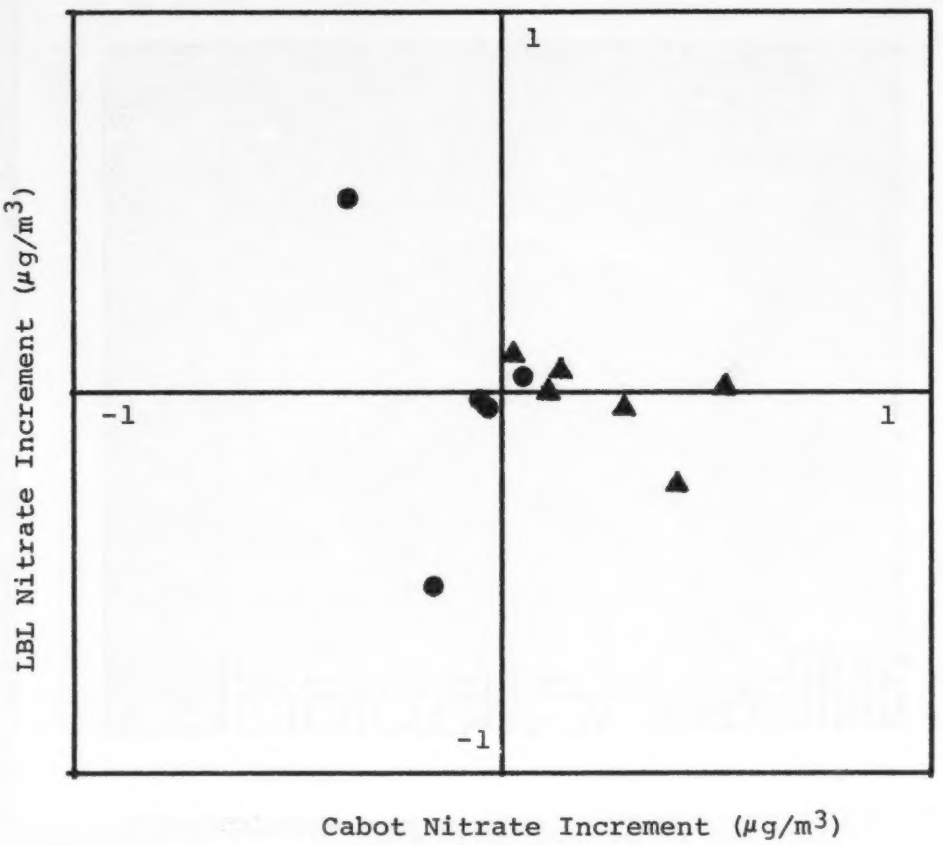


Figure 17. LBL nitrate increment vs the Cabot nitrate increment. Samples collected October 1978.

$$y = 0.013\ \mu g/m^3 - 0.28x$$
$$r^2 = 0.086$$

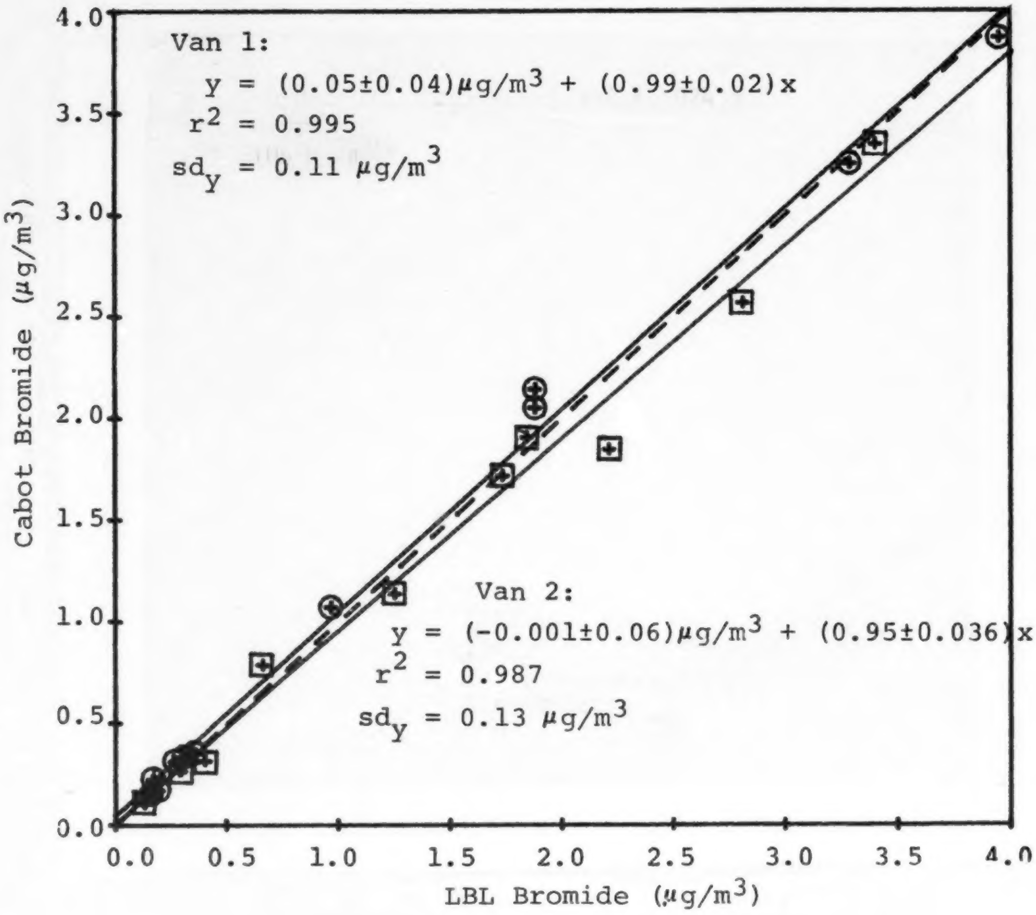


Figure 18. Comparison of bromide concentrations as determined from filter samples collected with the Cabot and LBL dichotomous samplers in the same van. Samples collected in October 1978.

⊕ - Van 1

⊞ - Van 2

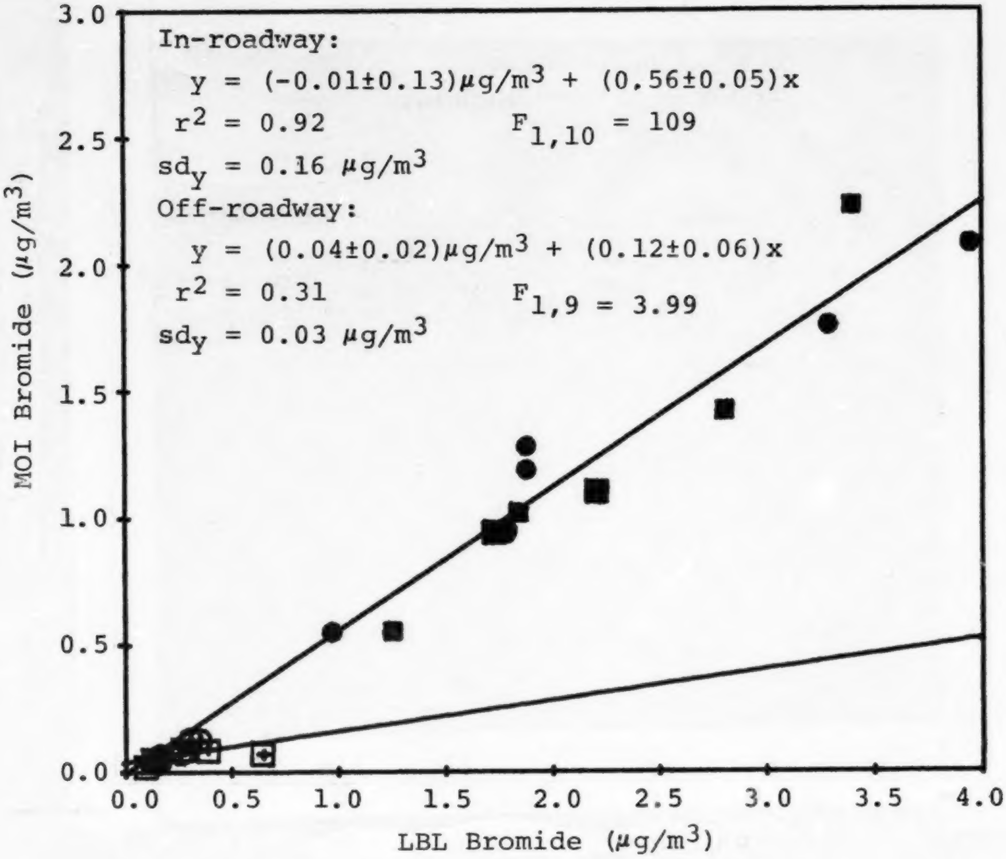


Figure 19. Micro-Orifice Impactor bromide vs the LBL bromide. Samples collected October 1978.

	In-roadway	Off-roadway
Van 1	●	⊕
Van 2	■	⊞

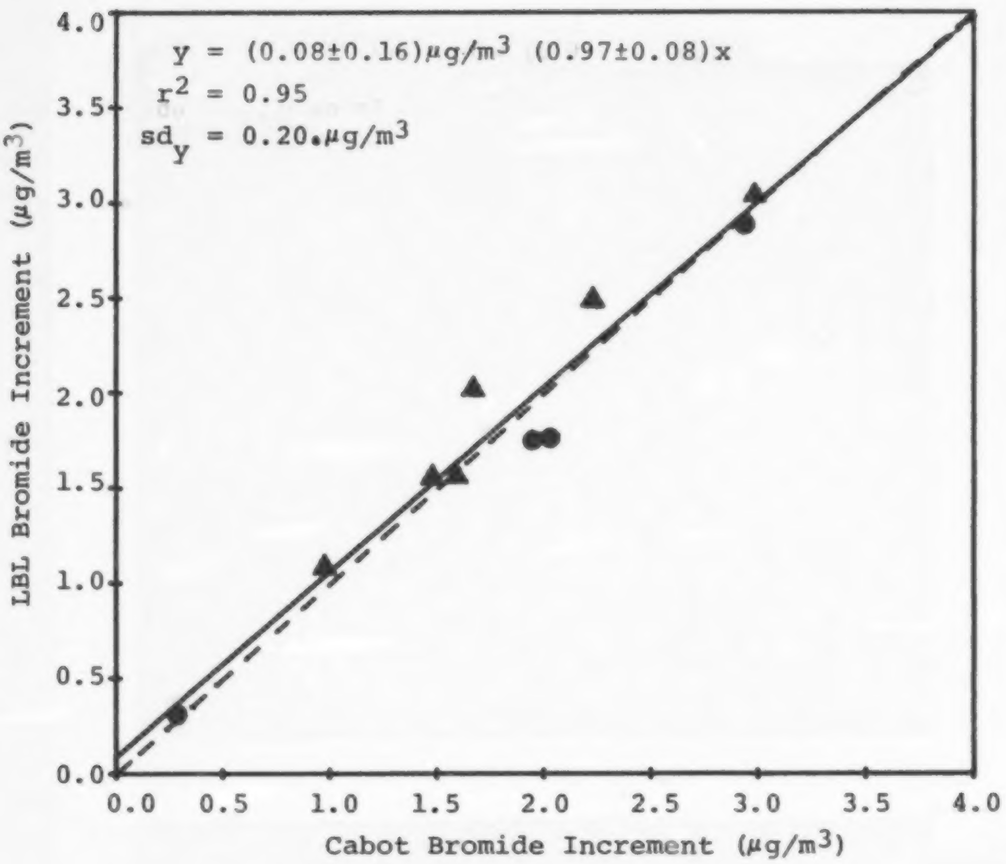


Figure 20. LBL bromide increment vs the Cabot bromide increment. Samples collected October 1978.

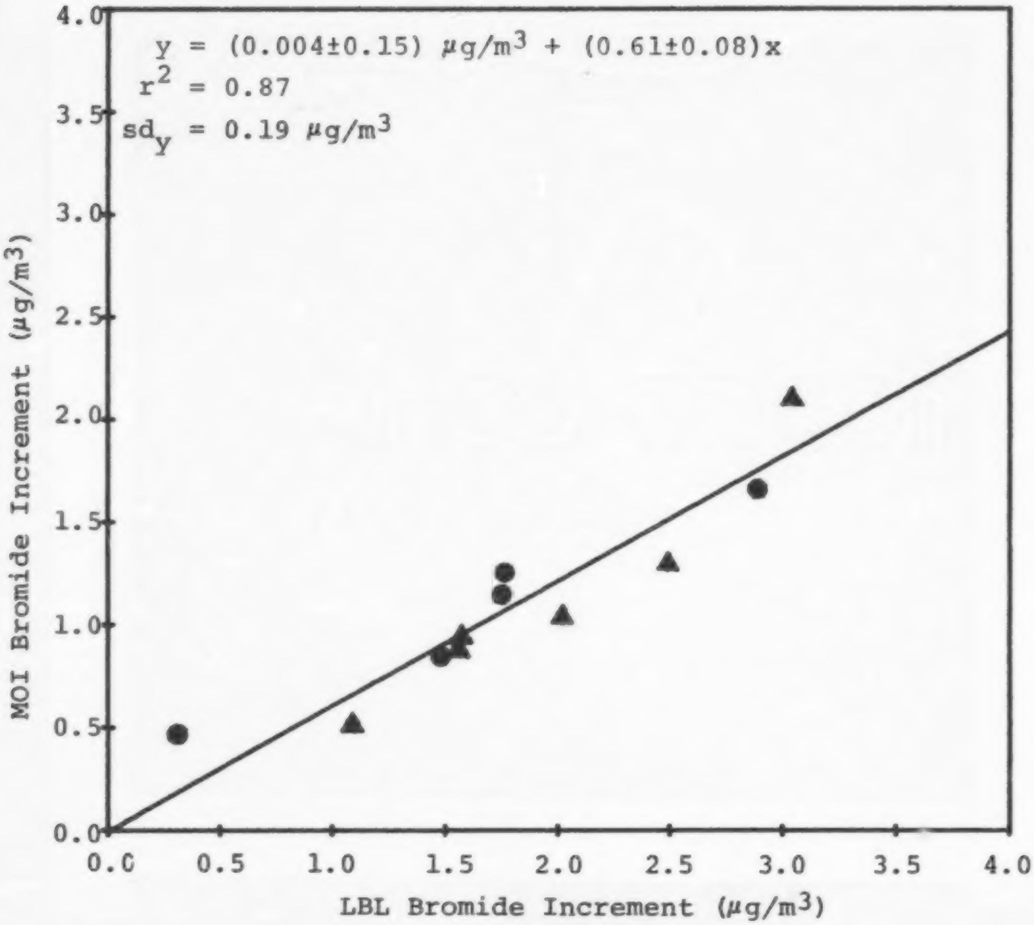


Figure 21. Comparison of bromide increment concentrations as determined with filter samples from the LBL and MOI samplers. Samples collected October 1978.

● Van 1 In-roadway, Van 2 Background

▲ Van 2 In-roadway, Van 1 Background

not complete, so that the values reported here are generally too small.

4.2.4 Lead Data

The aqueous extracts from the LBL and MOI filters were analyzed for lead by atomic absorption (AA). Subsequently, the LBL filters were again extracted with 10 percent nitric acid to be sure that all the lead was recovered, these extracts were analyzed for lead, and the results from the two extractions combined. On the average, about 40 percent of the observed lead was found in the second extraction. Here again, a comparison with XRF data discussed in Section 4.3.6 shows that even with the second extraction by nitric acid, the recovery of lead is not complete and the data reported here are low. The data from the LBL filters are reported in Table 12.

The roadway increment for lead has been compared to the roadway increment for bromide in Figure 22. The correlation between the lead and bromide is significant; however, the magnitude of the Pb/ Br ratio, 1.4, is smaller than the values near 2.5 reported in previous studies. This is in agreement with the finding discussed in Section 4.3.6, that these values are too small.

Table 12. Average Lead Concentrations (ug/m3) Determined from Filters Collected with the LBL Dichotomous Sampler and a Two-Stage Extraction into Water Followed by 10% Nitric Acid. Samples Collected October 1978. (Standard deviation about the mean is shown in ( ).)

	LBL
Total In-roadway	2.43(1.15)
Total Background	0.41(0.15)
Net In-roadway Increment	2.02(1.13)
Number of Observations	12

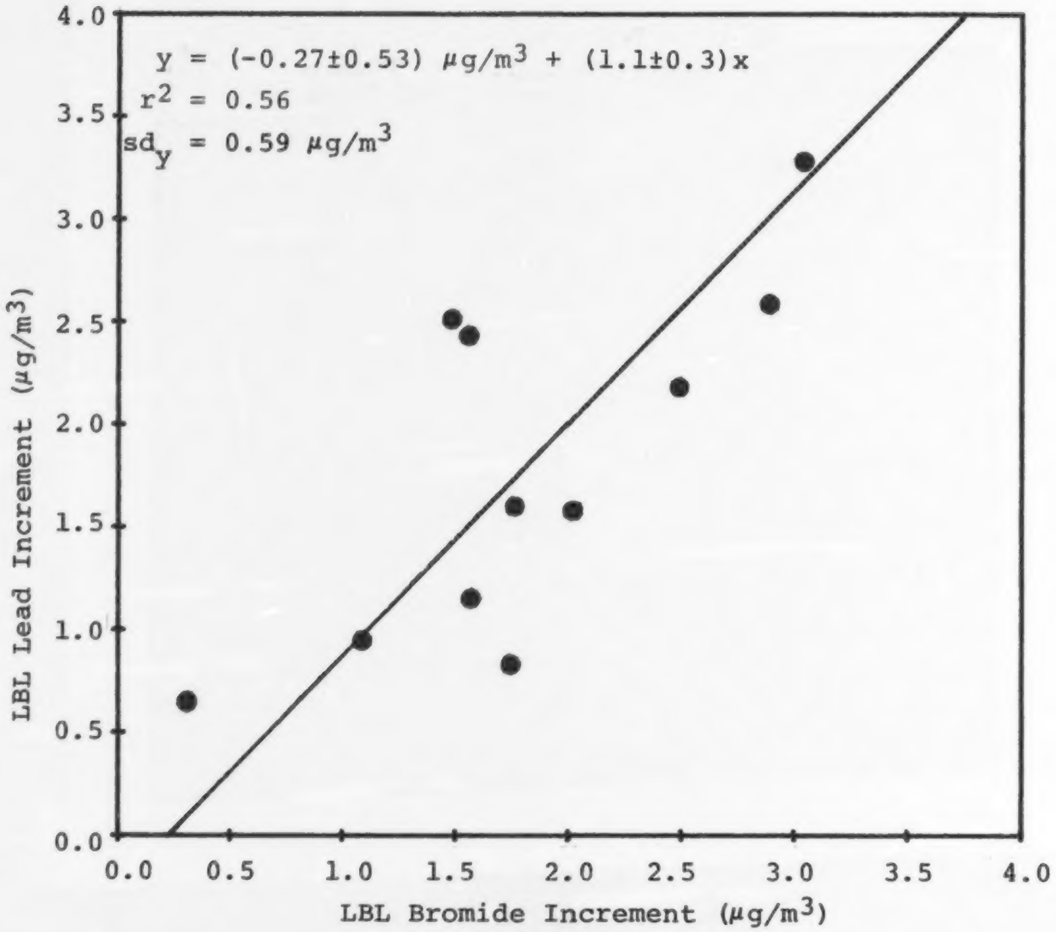


Figure 22. Comparison of the in-roadway minus the off-roadway increments of lead and bromide from particulates collected with the LBL dichotomous sampler. Samples collected October 1978. (These lead data are too small, due to incomplete extraction.)

4.2.5 Comparison of Sulfate, Lead and Bromide Data

Figures 23 through 25 show scatter diagrams comparing the in-roadway increments of sulfate to those of bromide and lead. It is a surprise that there is no correlation between the sulfate increment and the lead or bromide increments.

It is known that vehicles which emit lead have essentially no sulfate emissions, and that vehicles which emit sulfate release almost no lead. Therefore, in a series of samples collected in individual vehicle plumes, there should be a strong anti-correlation between lead and sulfate. On the other hand, when the sampling is carried out in such a way that it contains a composite of a great many vehicles, and the variability in the data is due to meteorological variations or traffic density variations, then a strong positive correlation between sulfate and lead increments would be expected.

It was believed that these one-hour samples were collected for a long enough period of time to average over a great many vehicles, so that the latter case should apply. However, this small set of data suggests that even in a one-hour sample collected while driving with the traffic on the roadway, the number of vehicle plumes sampled is small enough that a correlation between lead and sulfate does not appear in the data. The lack of correlation in the data is believed not to be due to the incomplete extraction of the lead.

These data support the view that the statistics of individual plumes are important in determining in-roadway exposure of people, and that surrogate calculations based on lead data should be performed with caution.

4.2.6 Sulfur Dioxide Data

In October, only one vehicle was equipped with a sulfur dioxide monitor, so that the in-roadway/off-roadway differences were calculated from data taken at different times during the day. On three different days, a total of six hourly average in-roadway measurements and six hourly average background measurements were taken. For the six determinations, the average in-roadway concentration was 15.9 ± 2.7 ppb; the average background was 3.7 ± 2.9 ppb; resulting in the average in-roadway increment of 12.2 ppb SO_2. With the calibration and the baseline drift for the Meloy SA-185 taken into account, the estimated error in the measured averages is about ± 4 ppb.

For each of the three days, the average in-roadway increment for SO_2 was compared to the average in-roadway increment for sulfate to determine the percentage of the in-roadway sulfur increment in the form of sulfate. The results

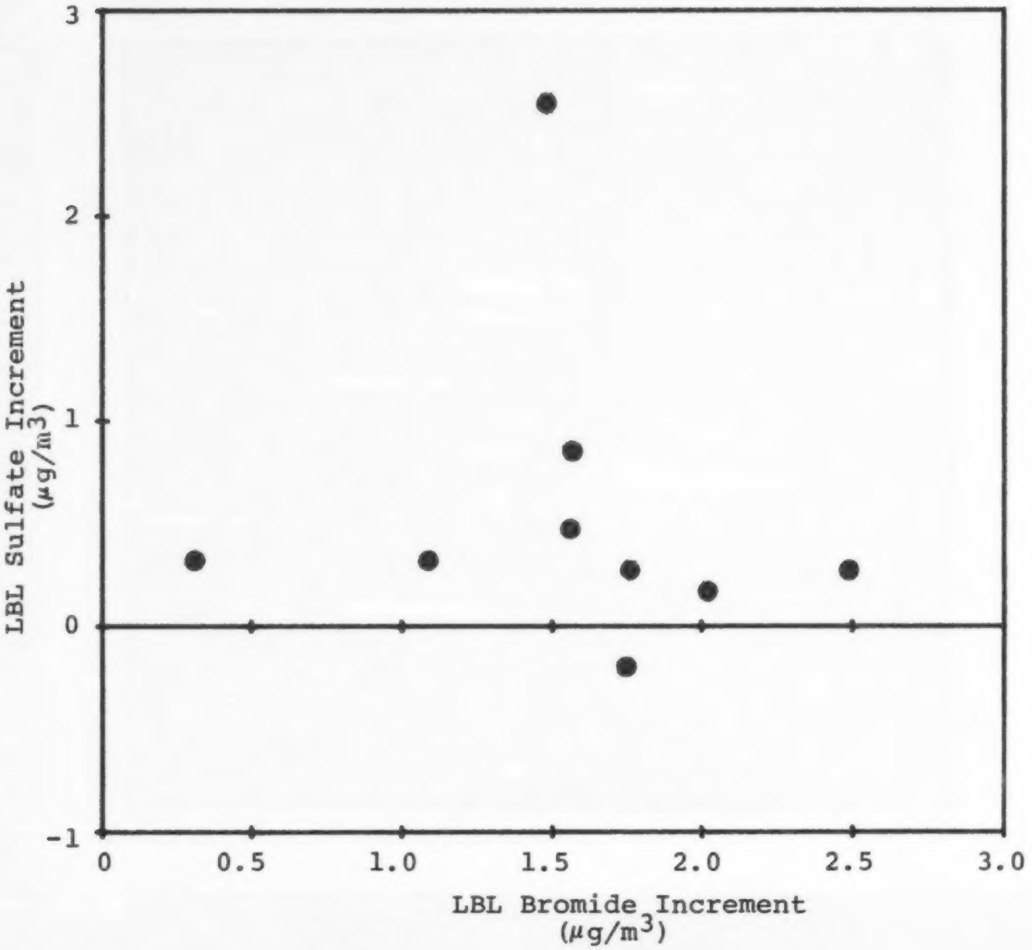


Figure 23. Comparison of the in-roadway bromide increment with the in-roadway sulfate increment for samples collected with the LBL dichotomous sampler. The F value for the correlation is 0.074 so that the probability that there is no correlation is 0.79. The samples were collected October 1978.

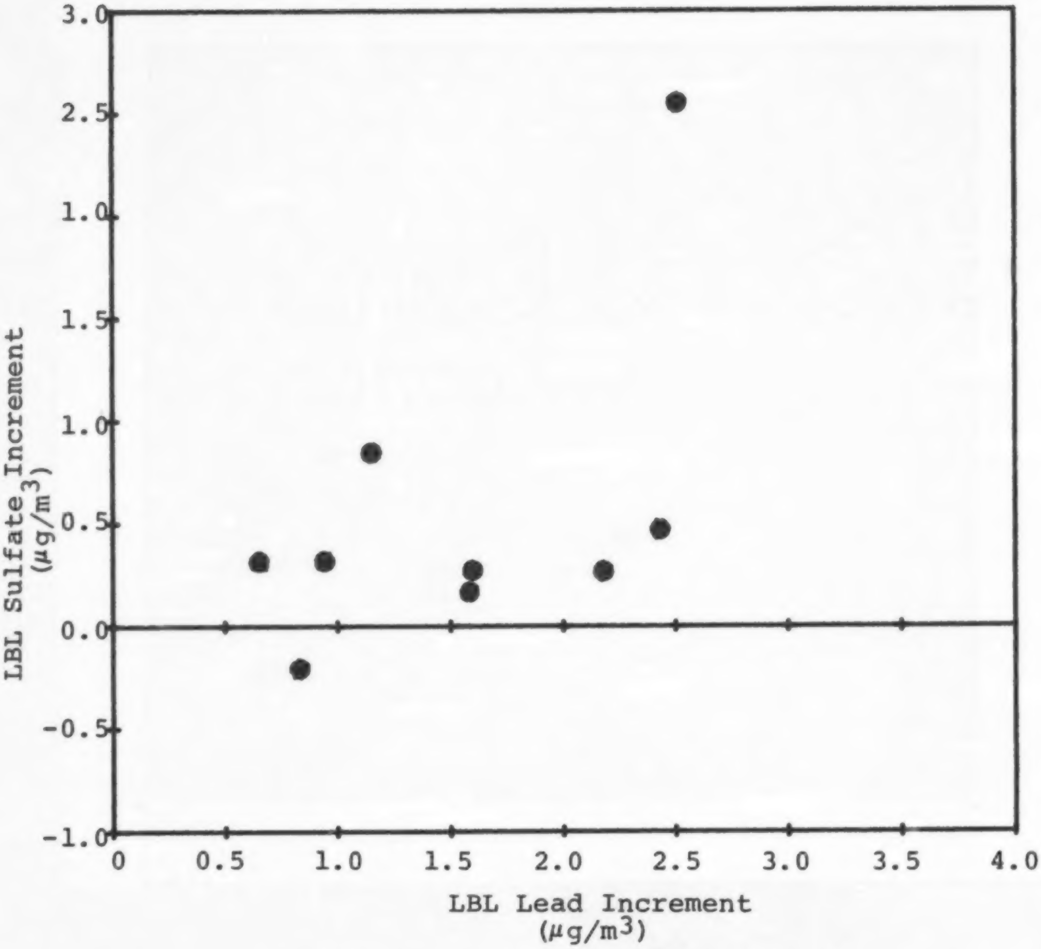


Figure 24. Comparison of the in-roadway lead increment with the in-roadway sulfate increment for samples collected with the LBL dichotomous sampler. The F value for the correlation is 2.8 giving the probability that the correlation does not exist as 0.13. The samples were collected October 1978.

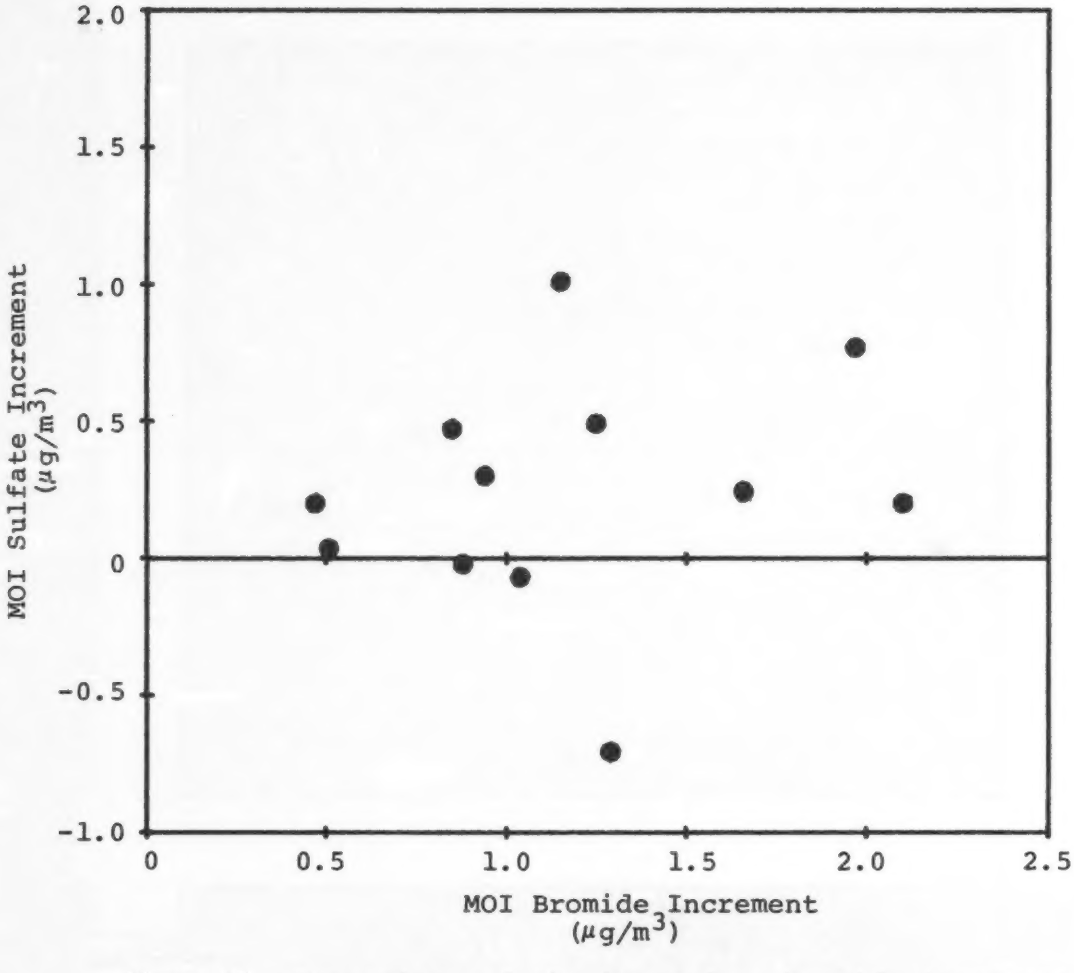


Figure 25. Comparison of the in-roadway bromide increment with the in-roadway sulfate increment for samples collected with the Micro-Orifice Impactor. The F value for the correlation is 0.37 giving a probability that there is no correlation of 0.56. The samples were collected October 1978.

of these calculations are presented in Table 13.

Table 13. Calculated Percentage of the In-Roadway Sulfur Increment in the Form of Sulfate

Date	Sulfate from LBL	Sulfate from MOI
10-18-78	3.3	0.6
10-23-78	0.5	0.3
10-30-78	2.7	1.5

4.2.7 Ammonia Data

Ambient ammonia was collected on glass fiber filters impregnated with oxalic acid after first passing through a Teflon filter to remove ambient particulates (including ammonium). The oxalic acid filters were extracted into buffer solution and the total ammonium determined with the indophenol colorimetric method.

A comparison of the in-roadway vs off-roadway ammonia concentrations is given in Figure 26. The average in-roadway minus off-roadway difference is 1.1 ± 1.9 ppb for six determinations, so that the standard deviation associated with the mean is 0.77. The 1.1 ppb is not significantly different from zero.

The motivation for making ammonia measurements, on and off the roadway, is to determine the concentration of the ammonia available to neutralize the sulfuric acid emitted by catalyst-equipped vehicles, and perhaps to determine the ammonia concentration changes due to the emission of ammonia by vehicles. The significant outcome of the ammonia data is that the average concentration of 10.6 ppb is 25 times the concentration necessary to fully neutralize the emitted sulfates assuming all the emitted sulfate is sulfuric acid. Small in-roadway ammonia increments appear in these data, but they are not statistically significant.

4.3 FEBRUARY 1978 MEASUREMENTS

The last series of in-roadway measurements on a congested freeway were made on the Ventura Freeway in the San Fernando Valley on February 5, 7, and 15, 1979. Generally, all sampling on the roadway took place between Topanga Canyon Boulevard, at the west end of the San Fernando Valley, and Laurel Canyon Boulevard. Background samples were collected simultaneously one

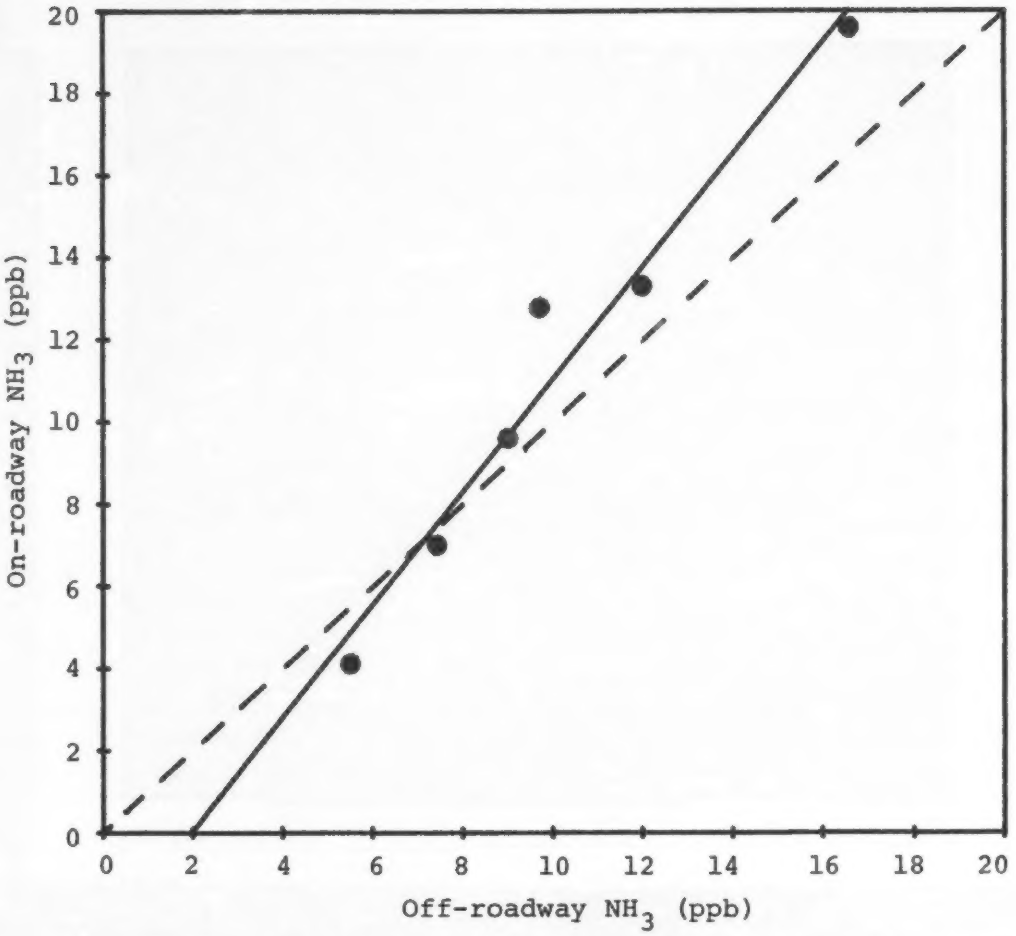


Figure 26. Comparison of in-roadway and off-roadway ammonia concentrations as determined from oxalic acid filter collection.

Regression line:

$y = (-2.7 \pm 1.5)\text{ppb} + (1.37 \pm 0.14)x$

$r^2 = 0.96$

$sd_y = 1.2$ ppb

or two miles upwind of the freeway on lightly traveled surface streets.

Micro-Orifice Impactor samples were collected for two hours instead of one hour in last October. The LBL samplers used in the October runs were returned to the EPA for modification and two different LBL samplers were installed in their place. In addition to the usual samples collected during these measurements, specially treated filters were used to collect aerosol while traveling behind a known catalyst equipped vehicle. These filters were used in the Cabot dichotomous sampler equipped with an ammonia denuder consisting of 3.8 cm diameter by 7.62 cm long CELCOR ceramic unit coated with phosphorous acid. These samples were collected for five minutes, then placed in a sealed container with oxalic acid (to preserve any collected sulfuric acid from ambient ammonia), and analyzed by low temperature volatilization for volatile sulfur species at 130°C.

Visual vehicle counts were conducted from the sampling van during the collection of the filter samples. The decision as to whether or not a car was catalyst equipped was aided by the fact that California license plates are issued sequentially, with the three numbers varying most rapidly, and the three letters varying most slowly. The first of the three letters on the license plate indicates within a month or two when the car was registered in California. This letter N for cars registered in the fall of 1974, when catalyst equipped cars began to appear. Therefore, cars for which this letter is earlier in the alphabet do not have catalysts. Cars for which this letter is later in the alphabet may not have catalysts if they are older cars brought in from other states, cars which do not require catalyst to comply with the emission requirements, etc. Most of these exceptions are fairly easily spotted, so that the estimates of the fraction of vehicles equipped with catalysts should be within a few percent of being correct.

Weather conditions on February 5 remained constant throughout the sampling period. The wind was from the north with occasional heavy to moderate gusts. It was a sunny day with clear blue skies. The visibility in the sampling area remained excellent throughout the day. Some haze developed at the extreme eastern end of the valley as the day progress, but this remained in the eastern end of the valley. On February 5, the fraction of catalyst equipped cars varied from one filter set to the next, with values ranging from 34 to 50 percent of the total vehicular traffic. Heavy duty gasoline powered trucks ranged from 1 to 5 percent of the total traffic while the fraction of diesel powered vehicles remained relatively constant at 4 ± 1 percent of the total traffic.

Two days later, on February 7, the conditions had changed dramatically. Visibility in the San Fernando Valley was poor; it was impossible to see the mountains at the northern end of the valley. There was a grayish haze covering the entire area. By late afternoon, the visibility was less than 7.4 miles (the distance between DeSoto at Route 101 and the Busch Brewery). The wind was very light and almost non-existent. Any light wind that did develop came out of the west. Throughout the day, catalyst equipped cars accounted for 43 percent of the traffic on the average, and the individual counts ranged from 35 to 50 percent. Heavy duty gasoline powered trucks accounted for 5 to 6 percent and diesel vehicles from 3 to 9 percent of the total traffic.

The last day of in-roadway sampling, February 15, was characterized by light haze in the morning and light winds from the west. The visibility was good in the morning; the mountains north of the San Fernando Valley were easily visible; however, the visibility began to deteriorate in the afternoon to the point where on the fourth filter set the mountains were barely visible at a distance of twelve miles. The number of catalyst equipped cars was fairly constant and ranged from 40 to 50 percent of the total traffic with an average of 45 percent. Heavy duty gasoline powered trucks accounted for 4 to 5 percent and diesel traffic for 9 to 12 percent of the total traffic. The increase in diesel truck traffic occurred as a result of the closure of the Pacific Coast Highway for repairs so that the traffic that normally used that route was now using the Ventura Freeway. On the previously sampling days, the average speed on the freeways was between 55 and 66 mph. On the 15th, the average speed varied from 40 mph for filter set 1, 44 mph for set 2, 55 to 65 mph for set three, and 48 mph for set 4. The decrease in the average speed was due to the increased traffic caused by the closure of the Pacific Coast Highway.

4.3.1 Sulfate Data

Prior to the extraction and analysis of the sample filters by ion chromatography, a new cation exchange column was purchased from the Dionex Company specifically for these analyses. It was hoped that the new column would improve the analytical precision for sulfate, nitrate, and bromide at the low levels encountered in one hour sampling. Based on the information given below, it appears that this was achieved. In this set of data, the standard deviation associated with side-by-side samples is almost a factor of two less than obtained in October.

The sulfate data from the Cabot and LBL dichotomous samplers are compared in Figure 27. There is an indication of a significant bias between the two samplers. This bias is also paralleled in the nitrate and bromide data. The flow rate through the Cabot sampler is monitored on-site and should not deviate by more than 5 percent. Before the new LBL samplers were installed, the flow rate was set at 50 l/m using a mass flowmeter with a low pressure drop. A check of the LBL total flow rate on 5 April 1979 indicated no significant change in the LBL total flow rate. This bias between samplers is not due to changes in the calibrated flow rate. It should be noted that this bias is the same in both vans to within the experimental error.

Table 14. Average Sulfate Concentrations in ug/m3
Segregated by Sampler for Data Collected in February 1979.
(The standard deviation is given in ( ).)

	LBL	Cabot	MOI
Total In-roadway	4.00(3.03)	5.16(3.27)	1.15(0.61)
Total Background	3.61(3.34)	4.75(3.95)	0.92(0.84)
Net In-roadway Increment	0.39(0.56)	0.40(0.84)	0.23(0.29)
Number of Observations	11	10	6

The sulfate results for all three days are given in Table 14. The values for the sulfate increment shown here are not significantly different from the values obtained in October 1978 at the 60 percent confidence level. (They are significantly different at the 50 percent confidence level.) The sulfate increment determined by the MOI agrees very well with the increment observed in October, which was 0.24 ug/m^3. The sulfate values obtained on the 5th and 15th only, which are days with a relatively low background sulfate concentration, result in in-roadway increments which are statistically significantly different from zero, as shown in Table 15. These values are in agreement with the October data; they are not significantly different at the 50 percent confidence level. (They are significantly different at the 40 percent confidence level.)

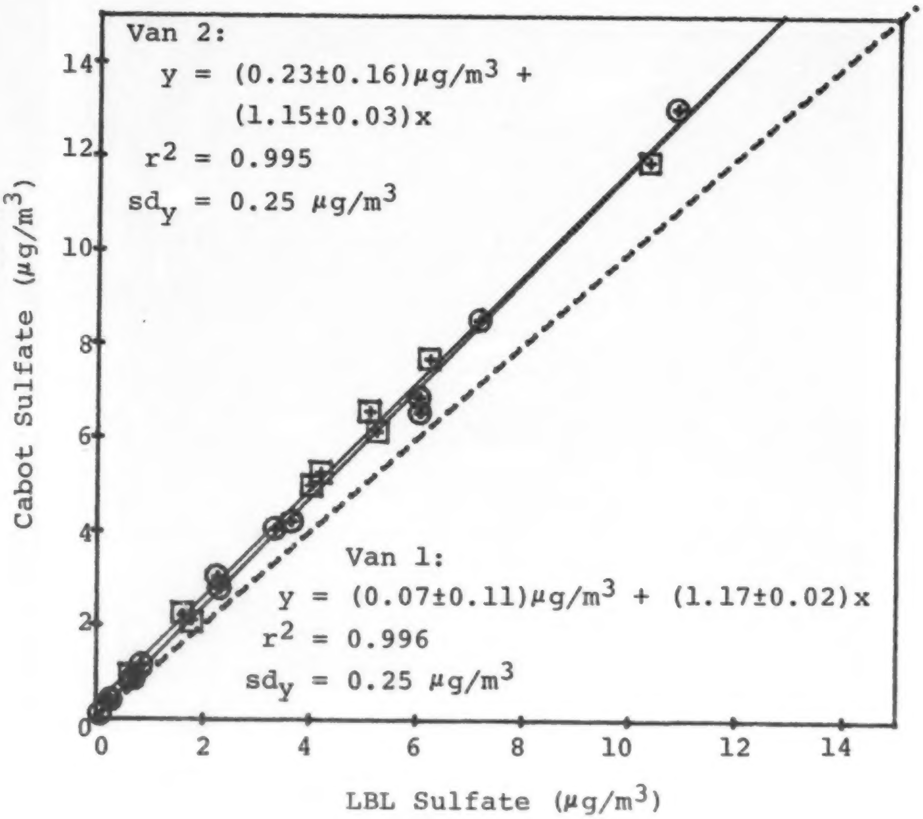


Figure 27. Comparison of sulfate concentrations as determined from filter samples collected in the same van in February 1979 with the Cabot and LBL dichotomous samplers.

⊕ - Van 1

⊞ - Van 2

Table 15. Average Sulfate Concentration in ug/m3 Segregated by Sampler for Data Collected on 5 and 15 February 1979. (The standard deviation is shown in ().)

	LBL	Cabot	MOI
Total In-roadway	2.17(1.52)	3.11(1.73)	0.82(0.43)
Total Background	1.61(1.46)	2.22(1.68)	0.43(0.47)
Net In-roadway Increment	0.56(0.17)	0.88(0.34)	0.39(0.18)
Number of Observations	7	8	4

The increased precision in the analysis of the filters collected in February has resulted in better agreement between the LBL and Cabot samplers when comparing values for the in-roadway sulfate increment. The data are shown in Figure 28. The two points in the third quadrant were obtained on February 7, when the background sulfate was high (7-10 ug/m^3).

Samples collected on the 5th and 15th of February result in an average in-roadway sulfate increment of 0.72 ug/m^3. This value represents the amount of sulfate aerosol in the roadway due to vehicular sources in the accumulation plus nuclei mode size ranges. The data from the MOI, which has a 50 percent cut diameter of 0.09 um, gave a net in-roadway sulfate increment of 0.39 ug/m^3. This converts to (54 ± 15) percent of the in-roadway sulfate increment in the nuclei mode. Figure 29 shows the MOI in-roadway sulfate increment as a function of the Cabot in-roadway increment. The regression line has an intercept which is not significantly different from zero and a slope indicating (27 ± 8) percent of the sulfate increment is in the nuclei mode. A similar regression line comparing the LBL and MOI results in (34 ± 21) percent of the in-roadway sulfate increment is in the nuclei mode particle size range.

In total, the February data agrees nicely with the October data. The averages of all the October and February data combined appear in Table 16. This table includes quite a few data in which the background sulfate concentrations were high. It was shown in Section 4.1.2 that high background sulfate concentrations can interfere with the determination of the in-roadway increment because of the fluctuations in the background concentration over the distances separating the two vans making the measurements.

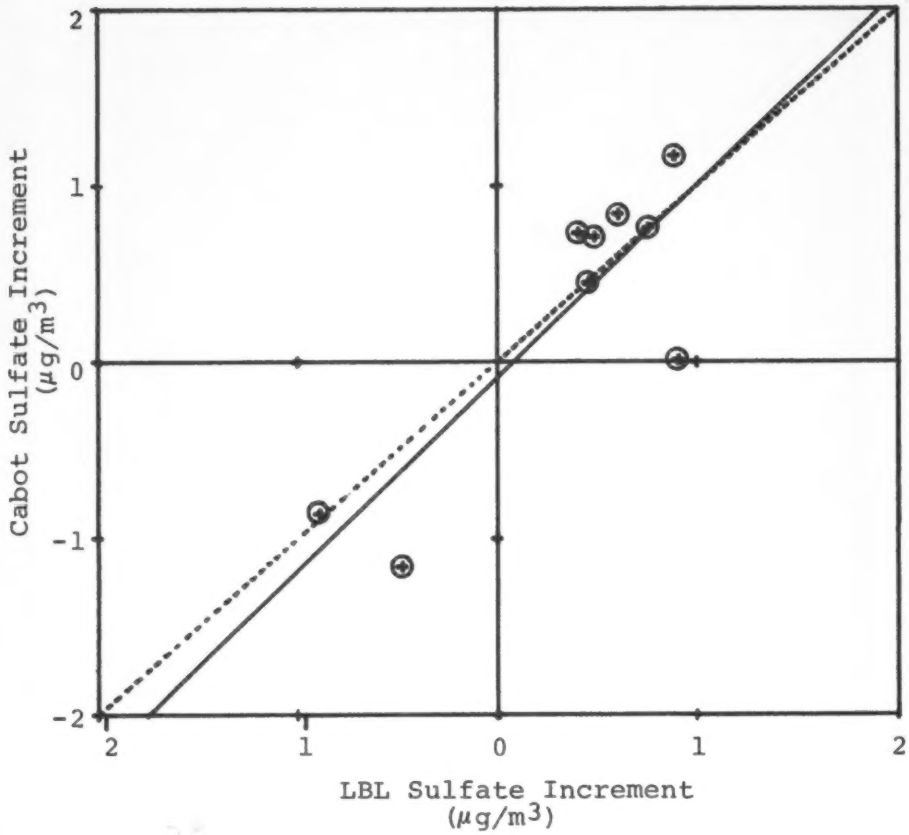


Figure 28. Comparison of in-roadway sulfate increments as determined from filters collected with the LBL and Cabot dichotomous samplers. The regression line is:

$$y = (-0.09 \pm 0.18)\mu g/m^3 + (1.09 \pm 0.26)x$$

with

$$r^2 = 0.71 \text{ and } sd_y = 0.46\ \mu g/m^3.$$

The samples were collected in February 1979.

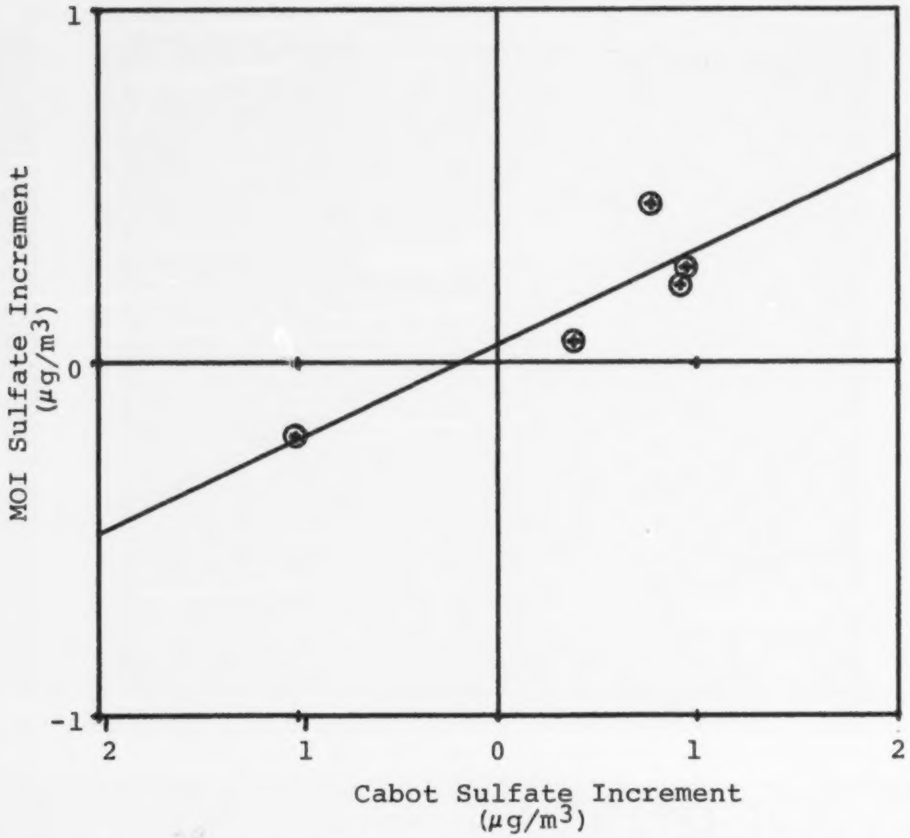


Figure 29. Comparison of in-roadway sulfate increments as determined from filters collected with the Cabot dichotomous sampler and the Micro-Orifice Impactor. The equation of the regression line is:

$$y = (0.05 \pm 0.07)\mu g/m^3 + (0.27 \pm 0.08)x$$

with

$$r^2 = 0.79 \text{ and } sd_y = 0.13\ \mu g/m^3.$$

The samples were collected in February 1979.

Table 16. Average Sulfate Concentrations in ug/m3 Segregated by Sampler for Data Collected in October 1978 and February 1979. (The standard deviation is shown in ( ).)

	LBL	Cabot	MOI
Total In-roadway	5.60(3.49)	6.31(3.50)	1.07(0.62)
Total Background	5.28(3.80)	5.68(3.65)	0.83(0.64)
Net In-roadway Increment	0.32(0.72)	0.63(1.02)	0.24(0.39)
Number of Observations	23	22	18

The data in Table 17 include results obtained only when the background sulfate concentration was less than 4.5 ug/m^3. The background concentration was less than this value on October 11 and 23; and February 5 and 15. On the basis of the data in Table 17, (36 ± 17) percent of the in-roadway increment sulfate is in the nuclei mode.

Table 17. Average Sulfate Concentrations in ug/m3 Segregated by Sampler for Data Collected on October 11 and 23, 1978; and February 5 and 15, 1979. (The standard deviation is shown in ( ).)

	LBL	Cabot	MOI
Total In-roadway	2.48(1.77)	3.11(1.91)	0.62(0.37)
Total Background	1.82(2.06)	2.23(1.53)	0.34(0.33)
Net In-roadway Increment	0.66(0.65)	0.88(1.11)	0.28(0.23)
Number of Observations	11	10	8

All of the filters collected with the LBL dichotomous sampler and the Micro-Orifice Impactor on February 7 were sent to the EPA for analysis by X-ray fluorescence. These filters were returned to the EMSC within one week and were then extracted and analyzed by ion chromatography. X-ray fluorescence detects elemental concentrations while the ion chromatograph is specific for sulfate. A comparison of the data obtained from these analytical methods on the same filter is presented in Table 18. These data show a clear trend, and suggest that the extraction efficiency of sulfate in the accumulation-mode particle size range may not be complete in the

Table 18. Comparison of Sulfate Concentration in $\mu g/m^3$ Determined from the Same Filter by Ion Chromatography and Total Sulfur Concentration as $\mu g/m^3$ Sulfate Determined by X-Ray Fluorescence

Filter	Sampler	Sampling Location[a]	IC $SO_4^=$ ($\mu g/m^3$)	XRF S as $SO_4^=$	Ratio IC/XRF
411	LBL	F	6.04[b]	7.92(0.56)[c]	0.76±0.06
413	LBL	F	6.06	7.17(0.56)	0.85±0.07
410	LBL	F	6.28	9.42(0.56)	0.67±0.05
411	LBL	F	10.39	13.14(0.56)	0.79±0.04
406	LBL	B	5.28	7.20(0.56)	0.73±0.06
408	LBL	B	5.15	6.93(0.56)	0.74±0.07
415	LBL	B	7.17	9.51(0.56)	0.75±0.05
417	LBL	B	10.87	13.38(0.56)	0.81±0.04
407	MOI	F	1.74	1.35(0.24)	1.29±0.28
416	MOI	F	1.87	1.62(0.24)	1.15±0.22
412	MOI	B	1.68	1.62(0.10)	1.04±0.15
409	MOI	B	2.08	1.89(0.10)	1.10±0.13

Notes: (a) F = in freeway; B = on nearby surface streets.

(b) The error in these values is estimated to be ± 0.22 $\mu g/m^3$.

(c) The error is indicated in parethenses.

ion chromatographic analysis. These data will be discussed more after the presentation of the lead and bromide data.

4.3.2 Sulfuric Acid Data

Samples were collected to be analyzed for sulfuric acid aerosol while traveling behind known catalyst equipped automobiles picked at random on the Ventura Freeway. The sampling times were five minutes. Teflon (TFE) membrane filters, treated with a saturated solution of DC-410 in acetone, were used in the Cabot dichotomous sampler. An ammonia denuder coated with phosphorous acid and made from a ceramic monolith 3.8 cm in diameter and 7.62 cm in length and containing 47 channels per square centimeter was used. These conditions were shown in the methods development work sponsored by the Coordinating Research Council (Richards and Johnson, 1980) to be optimum for the detection of sulfuric acid.

On the clean days, sulfuric acid was not detected. On the less clean days, signals like those from sulfuric acid were detected behind cars and also in the background. The presence of sulfur compounds in Los Angeles which can be collected on a filter and volatilized as if they were sulfuric acid has been noted previously (Richards, Wang, and Harker, 1977; Richards, et al., 1977, 1980; Kittelson, et al., 1978; Richards, Johnson, and Shepard, 1978). The fact that these compounds only partially lose their volatility on exposure to concentrated ammonia vapors argues that they are not predominantly sulfuric acid. The detection of sulfuric acid by the LTV method (or any method that depends on selective volatilization) in the presence of these compounds is difficult. In no case was sulfuric acid clearly detected behind a catalyst equipped car on the freeway. Sulfuric acid was clearly detected in the chase car experiments reported in the following chapter, so it is believed that the measurement method would have detected sulfuric acid had it been present at concentrations of a few micrograms per cubic meter.

4.3.3 Sulfur Dioxide Data

Sulfur dioxide was monitored continuously in both vans with flame photometric detectors manufactured by Meloy Laboratories. The linear output was recorded on strip charts and integrated to determine average sulfur dioxide concentrations corresponding to each filter sample set. The in-roadway increment for SO_2 varied little from set-to-set and averaged 11.7 ± 2.2 ppb regardless of the background SO_2 concentration. This agrees well with the average in-roadway increment determined in October of 12.2 ppb SO_2. A comparison of the average SO_2 increment with the data in Table 17 results in SO_2 to sulfate conversions of 1.4 percent for the LBL data, 1.9 percent for the Cabot data, and 0.6

percent for the MOI data.

4.3.4 Nitrate Data

The comparison in Figure 30 of the nitrate concentrations determined from filters collected with the LBL and Cabot dichotomous samplers shows the same bias as seen in the sulfate data. More material is collected with the Cabot sampler. The precision of the data as determined by the side-by-side sampling is almost a factor of two worse than that obtained in October. The fact that the filters were stored for a month and a half may have some bearing on the scatter in the nitrate data.

Average nitrate concentrations for the samples collected in February are given in Table 19. There appears to be a large and fairly significant deficit of nitrate on the roadway. This is caused primarily by the data collected on February 7, when background nitrate concentrations were large (9 to 15 ug/m^3), while in-roadway concentrations were consistently smaller. If the data of February 7 were omitted, the resulting increments would not be significantly different from zero.

Table 19. Average Nitrate Concentrations in ug/m3
Segregated by Sampler for Data Collected in February 1979.
(The standard deviation is shown in ().)

	LBL	Cabot	MOI
Total In-roadway	3.81(4.57)	5.07(5.44)	0.28(0.40)
Total Background	4.13(5.16)	5.87(6.31)	0.64(0.91)
Net In-roadway Increment	-0.32(0.93)	-0.80(1.43)	-0.36(0.52)
Number of Observations	11	10	6

4.3.5 Bromide Data

The comparison of the bromide concentrations in side-by-side samples collected with the LBL and Cabot dichotomous samplers in Figure 31 indicates a decrease in analytical precision in the data obtained in February compared to the data collected in October. The combination of the new analytical column used in the Dionex ion chromatograph and the length of time between sampling and analysis may account for the decrease in precision in the bromide and nitrate data. The average results for bromide are given in Table 20.

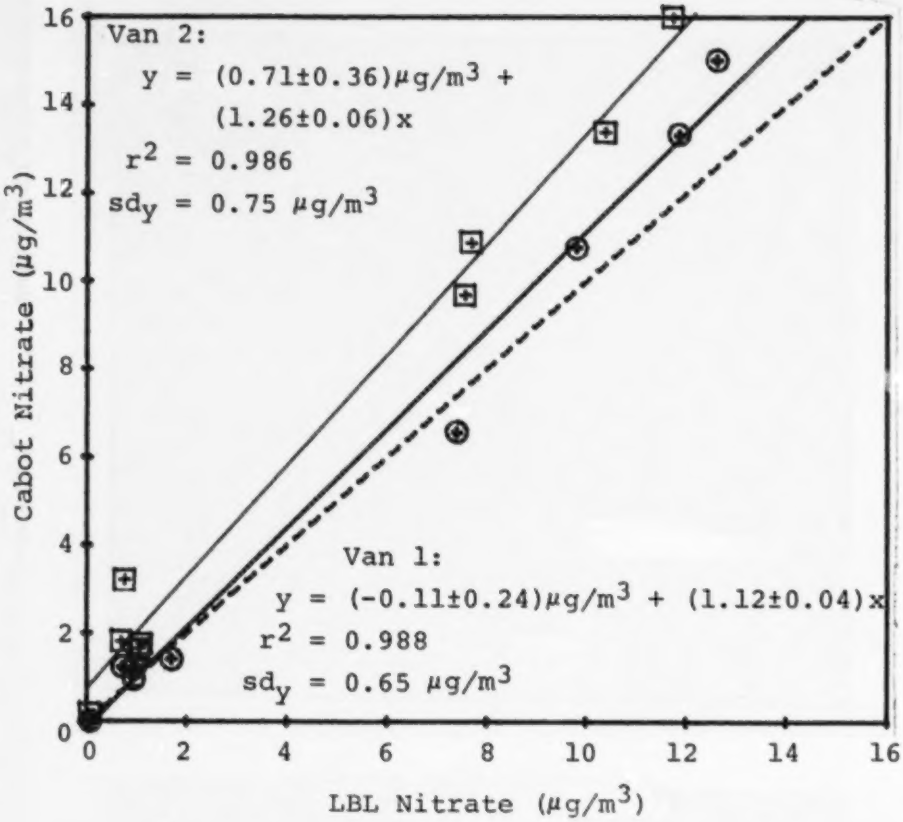
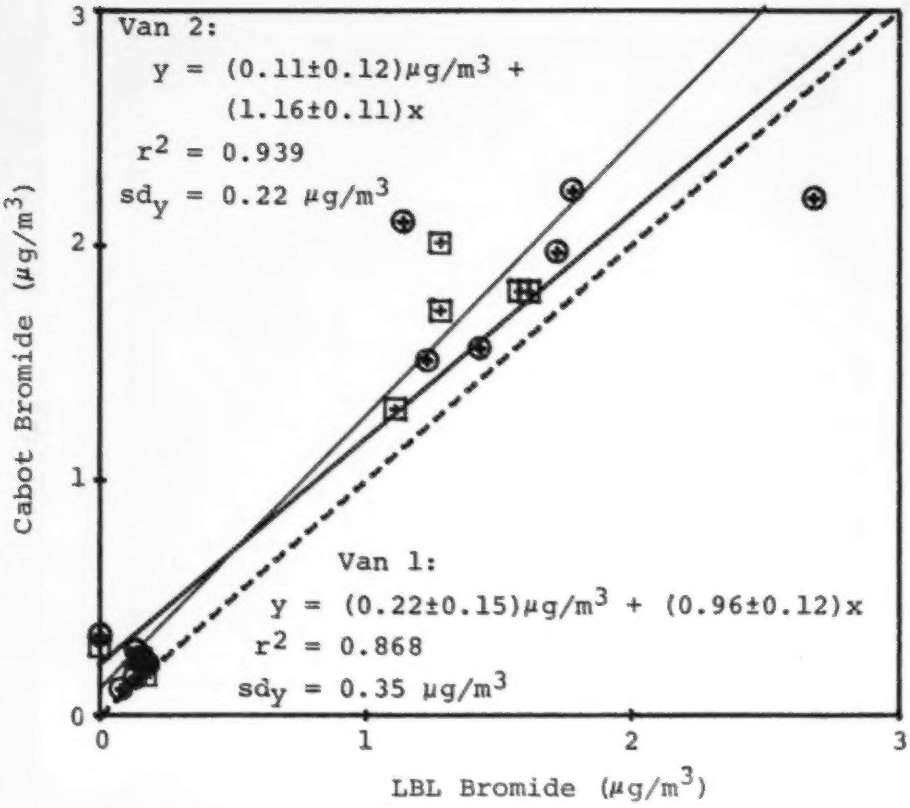


Figure 30. Comparison of nitrate concentrations as determined from filter samples collected with the Cabot and LBL dichotomous samplers in the same van. Samples collected in February 1979.

⊕ - Van 1

⊞ - Van 2



31

Figure 31. Comparison of bromide concentrations as determined from filter samples collected with the Cabot and LBL dichotomous sampler in the same van. Samples collected in February 1979.

⊕ - Van 1

⊞ - Van 2

Table 20. Average Bromide Concentrations in ug/m3 Segregated by Sampler for Data Collected in February 1979 and Determined by Ion Chromatography. (The standard deviation is shown in ().)

	LBL	Cabot	MOI
Total In-roadway	1.53(0.45)	1.85(0.30)	1.48(0.28)
Total Background	0.13(0.08)	0.22(0.07)	0.11(0.03)
Net In-roadway Increment	1.40(0.43)	1.64(0.29)	1.37(0.26)
Number of Observations	11	10	6

The average in-roadway bromide increment is higher in these data than in the data obtained in October; however, the difference is not significant at the 90 percent confidence level. A larger fraction of the bromide increment is in the nuclei mode in these data; 84 and 98 percent when derived from comparison with the Cabot and LBL dichotomous sampler data, respectively. A plot of the bromide increment for samples collected with the MOI as a function of the bromide increment for samples collected with the Cabot dichotomous sampler in Figure 32 results in a slope indicating (67 ± 37) percent of the bromide in-roadway increment in the nuclei mode.

The comparison of the Cabot in-roadway bromide increment as a function of the LBL in-roadway bromide increment in Figure 33 shows agreement that is within the precision of the analytical method.

A comparison of the data obtained by aqueous extraction followed by ion chromatographic analysis and the determination of bromine by X-ray fluorescence is given in Table 21. Either all of the bromine is not bromide, or the aqueous extraction does not recover all of the bromide. There is a consistent pattern in the fraction of the bromine which is recovered as bromide: For the nuclei mode size range, essentially 100 percent is recovered from the in-roadway samples, and about 50 percent from the samples collected at the background locations. For the small particle fractions from the dichotomous samplers (i.e., the accumulation mode plus the nuclei mode), about 50 percent is recovered from the in-roadway samples and only 24 percent from the background samples. Thus, it appears that in the fresh, very small particles, all the bromine is present as extractable bromide. However, as the particles coagulate and age, less and less of the bromine can be extracted and recovered.

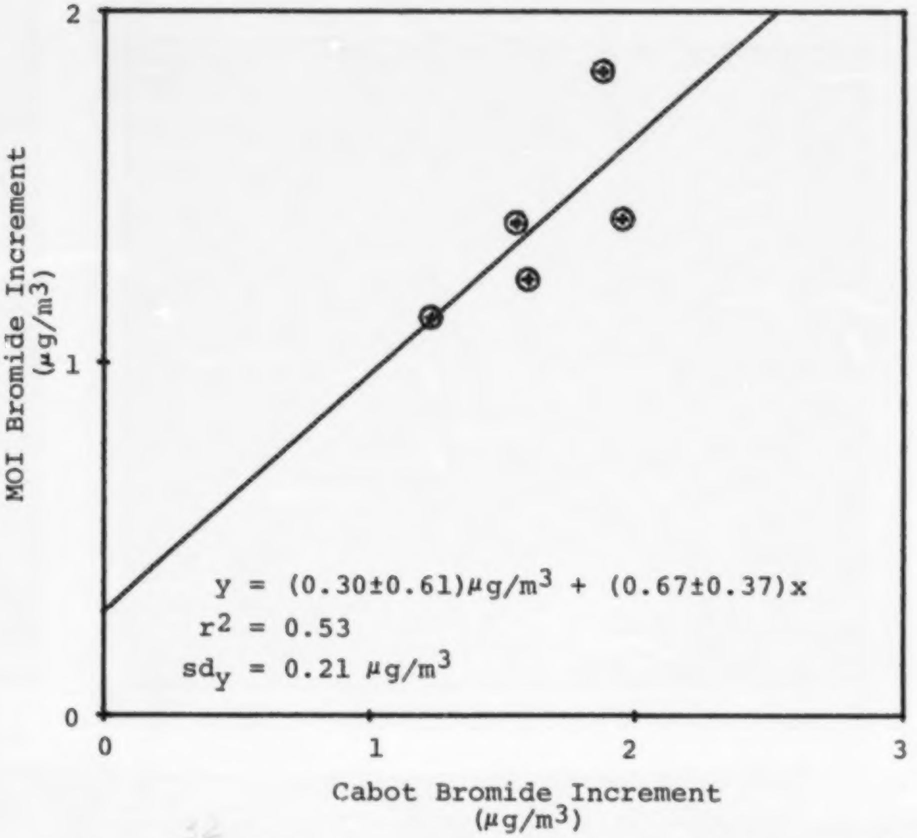


Figure 32. Comparison of in-roadway bromide increments as determined by ion chromatography from filters collected with the Cabot dichotomous sampler and the Micro-Orifice Impactor. Samples collected in February 1979.

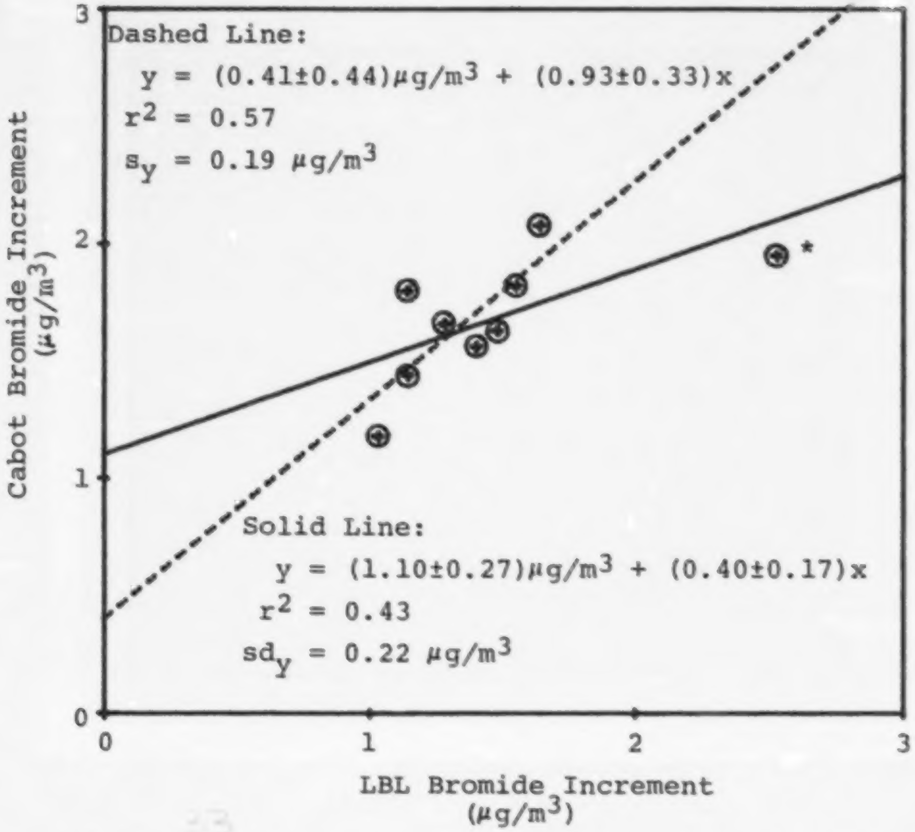


Figure 33. Comparison of in-roadway bromide increments as determined by ion chromatography from filters collected with the LBL and Cabot dichotomous samplers. Samples collected in February 1979. Dashed line represents the regression line with the outlier (*) omitted.

Table 21. Comparison of Bromide Concentration in $\mu g/m^3$ Determined from the Same Filter by Ion Chromatography and Bromine Concentration in $\mu g/m^3$ as Determined by X-Ray Fluorescence

Filter	Sampler	Sampling Location*	IC Br^- ($\mu g/m^3$)	XRF Br ($\mu g/m^3$)	Ratio IC/XRF
411	LBL	F	1.14(0.10)	3.31(0.15)	0.35±0.03
413	LBL	F	2.68(0.10)	3.59(0.15)	0.75±0.08
410	LBL	F	1.28(0.11)	2.77(0.15)	0.46±0.05
422	LBL	F	1.28(0.10)	2.91(0.15)	0.44±0.04
406	LBL	B	0.00(0.01)	0.75(0.03)	-
408	LBL	B	0.15(0.01)	0.56(0.03)	0.27±0.02
415	LBL	B	0.14(0.01)	0.65(0.03)	0.22±0.02
417	LBL	B	0.00(0.01)	0.70(0.03)	-
407	MOI	F	1.98(0.05)	2.03(0.08)	0.98±0.05
416	MOI	F	1.50(0.09)	1.59(0.08)	0.94±0.07
412	MOI	B	0.15(0.01)	0.28(0.01)	0.54±0.04
409	MOI	B	0.10(0.01)	0.20(0.01)	0.50±0.06

*F - in freeway; B = on nearby surface streets.

as bromide in the procedures used in this work.

When only the XRF data in Table 21 are used, it is estimated that 63 ± 6 percent of the in-roadway increment of bromine is in the nuclei mode particle size range. A summary of the bromine data obtained by X-ray fluorescence is given in Table 22.

Table 22. Average Bromine Concentrations in ug/m3 Determined by XRF. (The standard deviation is shown in ( ).)

	LBL	MOI
Total In-roadway	3.15(0.37)	1.81(0.31)
Total Background	0.67(0.08	0.24(0.06)
Net In-roadway Increment	2.49	1.57
Number of Observations	4	2

4.3.6 Lead Data

All filters were ultrasonically extracted with water at room temperature. Some of the filters were additionally extracted with nitric acid. Both the water extract and the nitric acid extracts were analyzed by atomic absorption for lead. The average results obtained are given in Table 23.

Table 23. Average Lead Concentrations in ug/m3 by Aqueous and Nitric Acid Extraction and Atomic Absorption Detection. (The standard deviation is shown in ( ).)

	LBL	MOI
Total In-roadway	2.44(2.25)	0.81(0.85)
Total Background	0.67(0.68)	0.01(0.01)
Net In-Roadway Increment	1.77(1.61)	0.80(0.84)
Number of Observations	4	4

The results from the filters collected with the LBL sampler are not significantly different from those obtained in October. The data in Table 23 indicate that (45 ± 10) percent of the in-roadway increment of small particle lead is in the nuclei mode. A comparison by linear regression between the MOI in-roadway increment as a function of the LBL in-roadway increments results in (48 ± 11) percent of the lead in the nuclei mode. These results do not compare favorably with the data obtained for bromide by ion chromatographic analysis.

Lead data by X-ray fluorescence are compared to the data obtained by aqueous and nitric acid extraction and atomic absorption analysis in Table 24. These data show that when significant amounts of lead are on the filter, only 50 to 60 percent is extracted. When the amount of lead on the filter is very low, as in the background MOI filters, the amount of lead extracted is almost insignificant. A comparison of the MOI in-roadway increment by XRF analysis (2.90 ± 0.38) $\mu g/m^3$, to the LBL in-roadway increment by XRF, (4.82 ± 0.62) ug/m^3, results in (60 ± 7) percent of the in-roadway increment of lead in the nuclei mode, which is in very good agreement with the fraction of in-roadway increment of bromine in the nuclei mode as determined by XRF.

The bromide data for filters collected with the LBL dichotomous sampler for the same filters as in Table 23 give an average in-roadway increment of 1.37 ± 0.58 ug/m^3. Therefore, the ratio of in-roadway increment lead to in-roadway increment bromide with extraction and analysis by atomic absorption is 1.28 ± 0.53, which is in agreement with the ratio under the same conditions as obtained in October (1.14 ± 0.34). The same comparison using only XRF data results in a ratio of 1.94 ± 0.72 which is, within error, the ratio of lead to bromine in lead chlorobromide.

These data show very clearly that the determination of bromide in ambient samples by aqueous extraction and ion chromatography, or the determination of lead by nitric acid extraction and atomic absorption, can lead to unsatisfactory results when Teflon filters are used. For bromine, there is the possibility that the results are partly due to the conversion of bromide to a different oxidation state, but no such explanation suffices for the lead data. In future experiments, the incompleteness of the extraction of lead and bromine from the filters could be demonstrated by XRF analysis of the filters after extraction.

The results obtained from the XRF data are internally consistent, and are consistent with other data for lead to bromine ratios in fresh automobile exhaust (Dzubay, Stevens, and Richards, 1979). They are summarized in Table 25.

Table 24. Comparison of Lead Concentrations in $\mu g/m^3$ as Determined from the Same Filter by X-Ray Fluorescence and Atomic Absorption (aqueous and nitric acid extraction). The Standard Deviation is in ( ).

Filter	Sampler	Sampling Location*	IC Pb ($\mu g/m^3$)	XRF Pb ($\mu g/m^3$)	Ratio IC/XRF
411	LBL	F	4.25(0.24)	7.63(0.34)	0.57±0.04
413	LBL	F	4.81(0.17)	7.90(0.34)	0.61±0.03
422	LBL	F	4.38(0.16)	7.31(0.34)	0.60±0.04
406	LBL	B	0.90(0.14)	2.64(0.12)	0.34±0.06
408	LBL	B	1.60(0.08)	2.28(0.12)	0.70±0.05
415	LBL	B	1.57(0.04)	2.60(0.12)	0.60±0.04
417	LBL	B	1.25(0.03)	2.93(0.12)	0.43±0.02
407	MOI	F	1.24(0.08)	4.00(0.17)	0.31±0.02
416	MOI	F	1.73(0.03)	3.33(0.17)	0.54±0.03
412	MOI	B	0.02(0.02)	0.83(0.04)	0.02±0.02
409	MOI	B	0.00(0.02)	0.70(0.04)	0.02±0.02

*F = in freeway; B = on nearby surface streets.

Table 25. Average Lead Concentrations in ug/m3 Determined by XRF. (The standard deviations are shown ().)

	LBL	MOI
Total In-roadway	7.61(0.30)	3.67(0.47)
Total Background	2.61(0.27	0.77(0.09)
Net In-roadway Increment	5.000	2.91(0.38)
Number of Observations	3-4	2

4.3.7 Ammonia Data

During the measurements conducted in February, ammonia was collected on oxalic acid impregnated filters in the van that was operating off the roadway. The results of these collections are given in Table 26. The collected efficiency was determined from the ratio of the amount of ammonium found on the second filter to the amount found on the first acid impregnated filter. As in all previous work, it was found that ammonia concentrations are many times those required to neutralize the sulfate emissions within the roadway. The strong excess of ammonia, and the failure to observe sulfuric acid, provided good evidence that any sulfuric acid emissions from catalyst equipped cars are neutralized within a few feet behind the emitting vehicle.

Table 26. Ammonia Concentrations in ppb Determined From Collection on Oxalic Acid Impregnated Filters

Date	Time of Day	Ammonia Concentration (ppb)	Collection Efficiency
2-5	morning	7.6 ± 0.5	0.92
2-5	afternoon	6.9 ± 0.5	0.92
2-7	morning	2.2 ± 0.3	0.87
2-7	afternoon	4.8 ± 2.0	0.36
2-15	morning	2.6 ± 0.3	0.82
2-15	afternoon	3.0 ± 0.3	0.92

5.0 THE CHASE CAR EXPERIMENTS

When this project began, it was planned to conduct chase car experiments near Research Triangle Park, North Carolina, with the following objectives:

- Measure the sulfate, sulfuric acid, and sulfur dioxide concentrations behind catalyst equipped vehicles to determine the rate of dilution of the exhaust.

- Compare in-roadway data with dynamometer data for vehicles having known, high sulfate emission rates to determine the comparability of the emission data obtained from the two measurement methods.

- Demonstrate the use of the low-temperature volatilization method for determining ambient concentrations of sulfuric acid.

The work was modified so that these experiments were conducted near Thousand Oaks, California. As a result, it was not possible to use a vehicle whose sulfate emission rates had been determined on a dynamometer. However, the logistics were greatly simplified, which permitted performing more experiments.

At the time these experiments were performed, it was known that the sulfate concentrations on Los Angeles freeways due to vehicle emissions were very small. Furthermore, it was known that the background ammonia concentrations were high enough on each day measurements were made to completely neutralize any sulfuric acid that may have been emitted before this acid could reach a following vehicle. Therefore, the objectives of the chase car experiments as they were performed were to:

- Measure the rate at which sulfuric acid is neutralized in the exhaust plume of an isolated catalyst equipped car.

- Measure the fraction of the emitted sulfate in the nuclei mode size range.

- Demonstrate the use of the low-temperature volatilization method for determining ambient concentrations of sulfuric acid.

Because of the existing SF_6 dilution rate data of Palmer and Shair (1977), it was only a minor objective to observe the rate of dilution of exhaust in the vehicle plume. No attempt was made to accurately determine the sulfuric content of the fuel and to operate the vehicle under well-enough characterized conditions that the sulfate emissions from these data could be compared with those from other studies.

The experiments were conducted on January 10, 17, 18, 25 and February 27, 1979, on the Simi Freeway, in Simi Valley, California.

5.1 EXPERIMENTAL EQUIPMENT AND METHODS

In the chase car experiments, one of the instrumented vans followed a new catalyst-equipped car on a freeway with low traffic densities. The experiments were conducted during the middle of the day, and rush hours were avoided. As far as possible, days with low sulfate backgrounds (good visibility) were selected. On some days, the second instrumented van measured background sulfate and ammonia concentrations at one nearby, upwind site.

In general, the instrumentation in the vans was the same as described in Section 3.1. However, for the experiments on and after January 17, 1979 the sampling intake was modified to be 30 to 45 cm above the ground (so that the emissions could be sampled close to the source). For the final day of sampling, February 27, 1979, a second Cabot Dichotomous Sampler and a second Micro-Orifice Impactor were added to the chase van. The sulfur dioxide measurements were made with a Meloy 185 sulfur gas analyzer with a Teflon filter on the sample inlet. The linear output was recorded on a strip chart and average sulfur dioxide concentrations determined by integration.

The vehicle used to generate the exhaust plume was an Oldsmobile Cutlass Cruiser, which is a "compact" station wagon. It was equipped with a Buick 231 cubic inch (3.8 l) V6 engine, air conditioning, and automatic transmission. The vehicle identification number was 3H35A9A432553.

The vehicle had been purchased by L.W. Richards in California in December 1978, and only fuel from pumps marked unleaded fuel had been used since the vehicle was received. The odometer readings increased from 656 to 740 mi during the runs on 10 January, and from 1955 to 2215 mi during the runs on 17 and 18 January. They increased from 3380 to 3637 mi on 27 February.

During the tests, t-butyl disulfide was added to the fuel as described in Table 27 to increase the sulfur content to approximately 0.3 percent, which is ten times the normal for unleaded fuels in Southern California (E.M. Shelton, 1977). The purpose of this was to make the sulfur dioxide and sulfate concentrations in the exhaust plume high enough so that useful data could be obtained. The Oldsmobile was deliberately allowed to run out of gas on each day before the experiments began so that the amount of t-butyl disulfide in the fuel would be known. No other attempt was made to determine the sulfur content of the fuel. A sulfur content in the purchased fuel anywhere between zero and twice the average would cause less than a 10 percent error in the estimated sulfur content of the fuel during the experiments. This uncertainty is small compared to the uncertainties arising from only partial preconditioning of the catalyst and a variable driving cycle. In the calculated emission rates in Table 27, the gasoline was assumed to originally contain 0.03 percent sulfur by weight.

Table 27. Volume of t-butyl Disulfide Added to the Gasoline Used in the Catalyst Equipped Vehicle for the Chase Car Experiments

Date	Volume Added per Gallon (ml/gal)	Average Miles per Gallon	Calculated Emission Rate (mg S/mile)	Calculated Emission Rate (mg S/km)
1-10	25.0	20.0	460	740
1-17	25.0	-	-	-
1-18	25.0	19.4	474	763
1-25	20.0	19.2	392	631
2-27	19.8	20.9	356	573

All analytical methods used on samples collected in the chase van were as previously described, including the use of DC-410 silicone polymer to pretreat the filters to be analyzed by volatilization into a flame photometric detector. The reason for adding a second Micro-Orifice Impactor for the February 27 experiments was to permit analyzing some filters from this collection device by volatilization and some by water extraction and ion chromatography. All filters to be analyzed for sulfuric acid were stored in the presence of oxalic acid immediately on removal from the sampler.

5.2 DATA FROM THE CHASE CAR EXPERIMENTS

5.2.1 Location and Sampling Days

The chase car experiments were conducted on the Simi Freeway between the Moorpark College exit and the Kuehner Drive exit, which are separated by 11 miles. Because of a grade near Moorpark College and the awkwardness of that exit, many runs were conducted between Kuehner Drive and First Street, which are separated by seven miles.

The first chase car experiments were performed on January 10, 1979. The sampling manifold intake was bout 1.7 m above the ground, in a position used for all previous in-roadway sampling. This and all subsequent runs were conducted at a constant speed of 55 mph. It was found that the sulfur dioxide concentrations were maximized at a distance of 25 to 35 m behind the emitting vehicle. Filter samples were collected at distances near the maximum concentration. The day was clear, and background sulfate concentrations determined by volatilizing filters at 190°C were 1 ug/m^3.

The second set of data was collected on January 17. The inlet to the sampling manifold was lowered to 30 to 45 cm above the pavement. With this configuration, very high SO_2 concentrations were measurable when traveling only 3 to 6 m behind the emitter. Aerosol samples were also collected at this close distance and submitted for sulfuric acid analysis by low temperature volatilization. Large amounts of sulfuric acid were recovered. The background sulfate concentration was less than 0.4 ug/m^3.

The following day, 18 January, extensive measurements were made at various distances behind the catalyst equipped car. Continuous SO_2 measurements were made along with the collection of aerosols. Also, particulates and ammonia gas were collected at the background site while the measurements on the roadway were taking place. The visibility was very good with background sulfate concentration of 0.73 ± 0.03 ug/m^3. The ammonia concentration measured at the background site was 6.6 ± 1.6 ppb.

Essentially the same measurements were made again on 25 January. On this date there was a strong wind from the west, resulting in excellent visibility and low concentrations of background pollutants. The background sulfate concentration was 0.33 ± 0.01 ug/m^3 and the ammonia concentration was 4.0 ± 1.6 ppb. The LBL dichotomous sampler was used for the first time in the chase car experiments to collect particulates along with the Cabot dichotomous sampler and the Micro-Orifice Impactor. Due to the strong winds, the SO_2 concentration dropped off more rapidly as the distance between the two vehicles increased than was observed in the previous experiments.

Based on the results of these measurements, and the fact that sulfuric acid was recovered in all measurements when traveling close behind the emitter, one final set of measurements was conducted in which the amount of data would be maximized. The instrumented van following the catalyst equipped car was equipped with an extra Cabot dichotomous sampler and Micro-Orifice Impactor, so that two of each as well as an LBL dichotomous sampler would obtain filter samples. These measurements were performed on February 27. This day started out with good visibility in the morning, which deteriorated in the afternoon and cleared up again by late afternoon. The background sulfate was 0.33 ug/m^3 in the morning and 0.66 ug/m^3 in the afternoon. Background SO_2 increased from 1.99 ppb in the morning to 5.3 ppb in the afternoon and decreased to 2.9 ppb in the late afternoon. Background ammonia averaged 6.3 ± 1.4 ppb.

5.2.2 Sulfur Dioxide Data

The sulfur dioxide concentrations observed during the chase car experiments are given in Table 28 and are plotted as a function of the distance behind the catalyst equipped car in Figure 34. The sulfur dioxide concentration during each run was determined from a strip chart record of the linear output of a sulfur gas analyzer. A Meloy Model 185 was used for the January measurements, and a Meloy Model 285 for the February measurements. The errors given in Table 28 are an estimate of the range in which the real concentration falls. The values for the Model 185 are based on numerous calibrations performed over months of constant use in other programs with the specific instrument used in these measurements. Therefore, the probability that the actual concentration falls within the range given, is high. The Model 285 used in these experiments has not had extensive field use, and the errors reported in Table 28 have been set at one half of those for the Model 185. These errors represent an absolute error with respect to the actual concentration; the relative error between measurements performed on the same day is probably on the order of 1.4 ppb.

The data taken 10 January illustrate the variations which can occur in the sulfur emission rates. The fuel had been spiked with sulfur and the catalyst equipped car had been running for at least one hour when the measurement at 1100 hours was made. At this time, the sulfur dioxide contributed by the automobile was approximately 9.5 ppb at a distance of 100 ft. After running out of gas, the car was refueled with spiked gasoline at 12:59. Approximately eight minutes later, the SO_2 concentration 100 ft behind the emitter was measured at 3.0 ppb. Eleven minutes later it was up to 4.1 ppb and 9 minutes after that, it was at 7.2 ppb; near the level measured in the

Table 28. Sulfur Dioxide Concentrations During the Chase Car Experiments.
Estimates of the concentration errors are given in ( ).

Date	Time	Distance Behind Emitter (m)	Sulfur Dioxide Concentration (ppb)
1-10	1100	30 ± 6	10.7(4.3)
	1110	Background	1.2(3.5)
	1307	30 ± 6	12.8(4.4)
	1318	30 ± 6	13.9(4.5)
	1327	30 ± 6	17.0(4.7)
	1339	Background	9.8(4.2)
1-17	1040	15 ± 4	31.7(5.8)
	1100	Background	1.4(3.6)
1-18	1543	Background	1.1(3.6)
	1552	15 ± 4	22.7(5.1)
	1556	29 ± 4	15.5(4.6)
	1607	59 ± 4	4.4(3.8)
	1616	88 ± 4	7.4(4.0)
1-25	1156	15 ± 4	19.1(4.9)
	1204	29 ± 4	9.3(4.2)
	1215	44 ± 4	4.2(3.8)
	1220	Background	0.9(3.6)
	1230	117 ± 4	1.1(3.6)
2-27	1249	Background	1.9(1.8)
	1310	15 ± 4	8.5(1.9)
	1331	88 ± 4	4.5(1.8)
	1356	59 ± 4	6.0(1.8)
	1418	29 ± 4	8.1(1.9)
	1433	15 ± 4	11.8(2.0)
	1445	Background	5.3(1.8)
	1528	29 ± 4	10.6(2.0)
	1548	15 ± 4	14.2(2.1)
	1603	29 ± 4	7.0(1.9)
	1615	59 ± 4	7.7(1.9)
	1631	Background	2.9(1.8)

Background in the distance column means that the measurements were made in front of the catalyst-equipped automobile acting as the emitter.

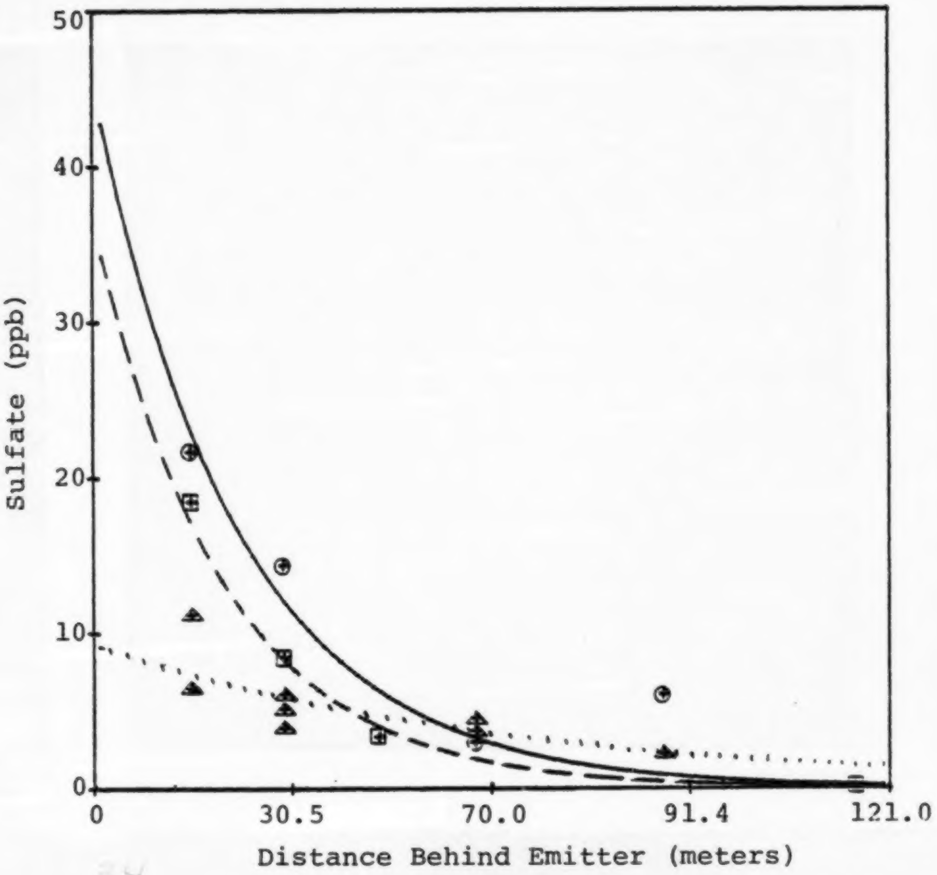


Figure 34. Sulfur dioxide concentration as a function of the distance between the catalyst equipped automobile and the instrumented van. The data points have been fitted by least squares to $y = a \exp(bx)$.

⊙ - Data from 1-18-79

⊡ - Data from 1-25-79

△ - Data from 2-27-79

morning.

The exponential dilution of the vehicle plume observed by Palmer and Shair (1977) is evident in the SO_2 data in Figure 34. Here the SO_2 concentrations have been corrected for the background readings. The faster dilution observed in the data of 25 January as compared to 18 January can be attributed to the gusty winds across the freeway on the 25th. They caused the samples to be collected nearer the edge of the plume as the distance between the vehicles increased. Measurements close to the emitting vehicle gave approximately the same results on both days with or without the wind.

One phenomenon that was observed on all days was a very high sulfur dioxide concentration peak behind the catalyst equipped vehicle when accelerating onto the freeway. This emission of sulfur dioxide generally lasted from 50 to 55 seconds with an average concentration of 95 ppb. Peak concentrations of sulfur dioxide during these accelerations averaged 430 ppb with some measurements as high was 725 ppb.

An average run on the freeway generally lasted ten minutes, after which time the vehicles would exit from the freeway and turn around for another ten minute sample run. The average sulfur dioxide concentration encountered behind the emitter during the ten minute run was approximately 10 ppb. Acceleration onto the freeway accounts for 100 ppb for one minute. Therefore, roughly half of the sulfur emitted in these experiments was emitted during acceleration onto the roadway. Filter samples were not taken during this period of acceleration. Some data for specific peak sulfur dioxide concentrations during acceleration are given in Table 29.

The non-steady driving pattern used in these chase car experiments, and the demonstrated wide variability in the sulfur dioxide emission rates, makes it unwise to attempt a quantitative interpretation of the observed emission rates. Instead, the data are interpreted from the point of view that the catalyst equipped car provided a realistic source of sulfates that made it possible to observe the dispersion and transformations of these sulfates in the atmosphere. However, to the extent that quantitative data are available they are presented.

5.2.3 Sulfate Data

All of the sulfate concentrations determined from filter collections are presented in Table 30. The data are tabulated according to the type of sampler and the analytical method used to determine the sulfate.

Table 29. Sulfur Dioxide Emissions During Acceleration onto the Freeway During the Chase Car Portion of LAFMMS

Date	Time	Time for Acceleration (min)	Peak SO_2 Concentration (ppb)	Average SO_2 Over the Acceleration Period (ppb)
1-10	1202	0.8	278	99
	1226	1.0	447	84
	1308	1.0	413	82
1-18	1556	0.8	725	145
	1604	0.7	229	61
	1612	0.8	540	93
1-25	1153	1.0	406	99
AVERAGE		0.87±0.13	434±165	95±26

Table 30. Results of Analysis for Sulfate on Teflon Filters
Collected During the Chase Car Experiments
Tabulated Values are $\mu g/m^3$

Date	Time	Distance Behind Emitter (m±4)	Cabot by LTV	LBL by IC	MOI by LTV	MOI by IC
1-10	1318	30			11.6(0.7)	
	1327	30	22.0(1.0)			
	1339	Background	1.2(0.1)		0.79(0.05)	
1-17	1040	15	79.0(4.0)	all sulfuric acid		
1-18	1552	15	52.0(6.0)		66.0(4.0)	
	1556	29	43.0(4.0)		34.0(3.0)	
	1607	59	11.0(2.0)		12.0(2.0)	
	1607	Background		0.73(0.03)		
	1616	88	5.0(2.0)		6.0(1.0)	
1-25	1156	15	30.0(6.0)	42.0(8.0)	40.0(3.0)	
	1204	29	13.0(4.0)	23.0(2.0)		
	1215	44	11.0(3.0)			
	1218	Background		0.33(0.01)		
	1234	117			6.0(1.0)	
2-27	1309	15	18.0(2.0)	25.9(0.8)	23.0(2.0)	
	1321	Background		0.33(0.01)		
	1330	88	10.0(1.0)	11.4(0.4)		
	1355	59		17.6(0.5)		
	1417	29		14.1(0.6)	5.0(1.0)	
	1432	15	14.0(3.0)	40.0(1.0)		
	1444	Background	4.0(2.0)			
	1527	29	10.0(2.0)	16.2(0.7)	7.0(2.0)	
	1528	Background		0.66)0.02)		
	1548	15		64.0(1.0)		68.0(1.0)
	1602	29		22.7(0.6)		24.9(0.8)
	1614	59		19.5(0.5)		21.0(0.7)
	1631	Background		1.06(0.06)		0.53(0.11)

Values in parentheses are standard deviations of analysis.

At a distance of 15 m behind the emitter, there are two comparisons between sulfate collected with the Micro-Orifice Impactor and analyzed by low temperature volatilization, and sulfate collected with the LBL dichotomous sampler and analyzed by ion chromatography. These two comparisons show that there is no significant difference in the determination of sulfate by volatilization or by ion chromatography under these sampling conditions. That is, at distances close to the emitter, (1) all of the emitted sulfate is in the nuclei mode, and (2) most, if not all, of the emitted sulfate volatilizes at 190°C and, therefore, is comprised of sulfuric acid, ammonium bisulfate, and/or ammonium sulfate.

A review of the data shows that the sulfate concentrations determined by the Cabot dichotomous sampler and volatilization analysis are significantly smaller than those from the LBL dichotomous sampler and ion chromatography. Because much smaller volumes were collected with the Cabot sampler, the volume of gas in the sampler ahead of the filter, which does not contain sulfate when the sampling is started, contributes to this discrepancy. However, most of the difference between Cabot and LBL sampler data arises from a lack of agreement between the two sulfate determination methods for accumulation mode particles.

To determine the fraction of the emitted sulfate in the nuclei mode size range, the sulfate data from the Micro-Orifice Impactor are compared to those from the Cabot and LBL dichotomous samplers in Figure 35. These data include all samples collected at distances up to 88 m. It appears that all of the sulfate is emitted and remains in the nuclei mode size range even at distances up to 88 m. The scatter in the data can in part be attributed to the small sample sizes and the dead volumes of the instruments, and in part to the differences in the analytical methods. On the basis of other data and the sampling times used in these experiments, the most reliable data would be expected to be obtained from the comparison of LBL dichotomous samplers and MOI data when all filters are analyzed by ion chromatography. There are only three such pairs of data, and they are shown in Figure 35 by the triangles, and shown as a function of distance in Figure 36. A least squares fit to these data gives

$$C_{MOI} = (0.77 \pm 0.44)\ \text{ug/m3} + (1.04 \pm 0.01)\ C_{LBL}.$$

There is no evidence for the emission of sulfate particles larger than the cut point of the MOI, nor for the emitted particles to coagulate with the accumulation mode background aerosol.

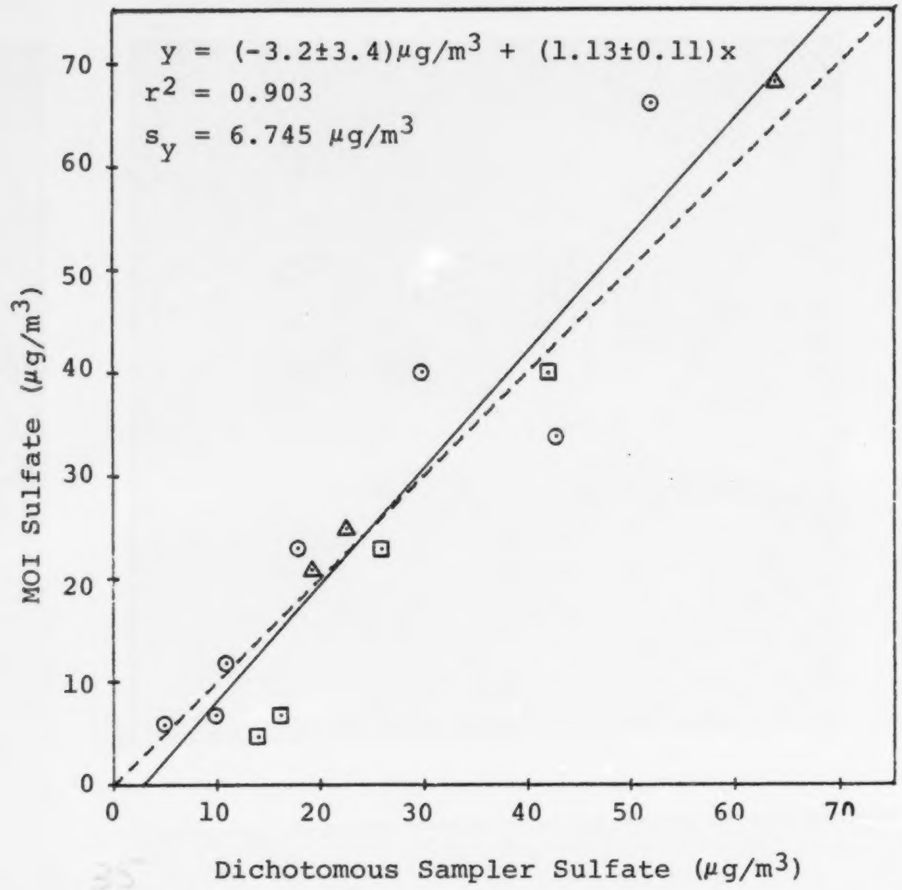


Figure 35. Comparison of sulfate concentrations determined from filters collected with the Micro-Orifice Impactor and sulfate concentrations determined from filters collected with Cabot or LBL dichotomous samplers.

⊙ - Cabot (LTV) vs MOI (LTV)
⊡ - LBL (IC) vs MOI (LTV)
△ - LBL (IC) vs MOI (IC)

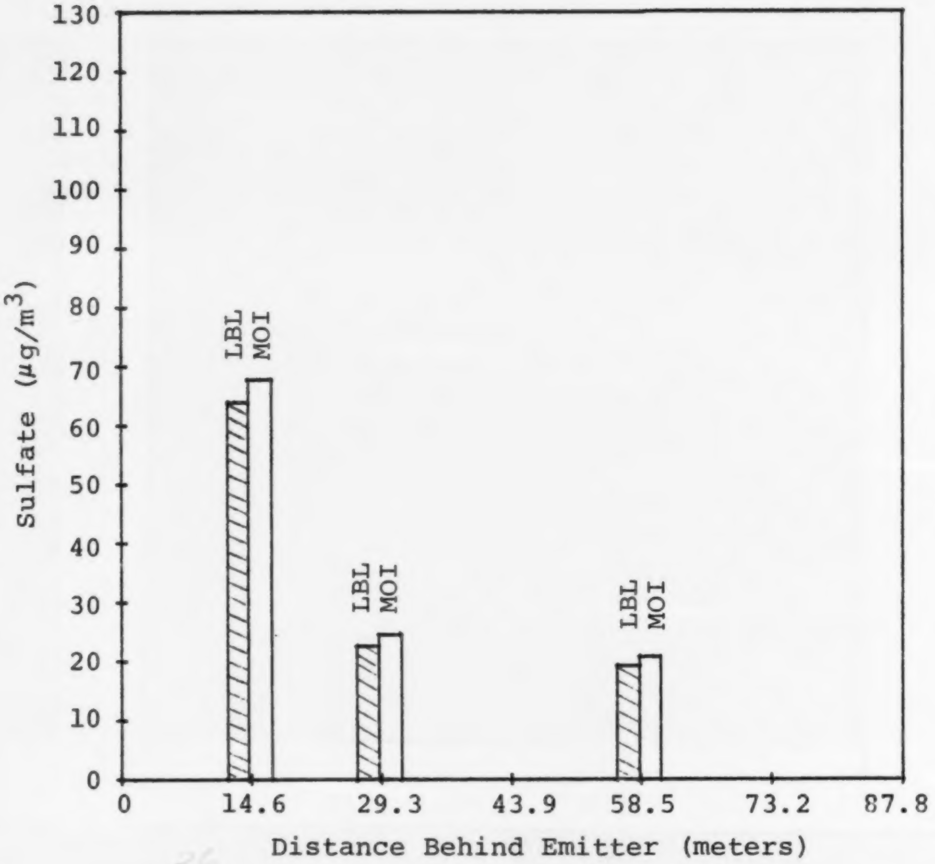


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Figure 36. Sulfate concentrations determined from ion chromatographic analysis of filter samples collected with the Micro-Orifice Impactor and the LBL dichotomous sampler at various distances behind the catalyst equipped vehicle.

5.2.4 Sulfuric Acid Data

Sulfuric acid concentrations behind the catalyst equipped car were determined by collecting the sulfuric acid aerosol on Teflon filters, then analyzing the volatile sulfur at 130°C. To prevent losses during collection by reaction with ambient ammonia, ammonia denuders were used to trap the ambient ammonia with the phosphorous acid as it diffused to the denuder walls. The filters were treated with Dow Corning DC-410 silicone gum in acetone solution. This treatment reduced some of the adsorption of the sulfuric acid on the Teflon. Immediately after the sampling period had ended, the filters were removed from the samplers and stored in airtight containers with oxalic acid.

In the laboratory, the filters were analyzed by low temperature volatilization into a flame photometric detector immediately after removal from the closed containers. The integrated response from the FPD was compared with the response of known quantities of sulfuric acid aerosol generated in the laboratory and collected on treated Teflon filters. At a temperature of 130°C, ammonium bisulfate, ammonium sulfate, and other inorganic sulfates are not volatile. Ambient particulates that contain species that will react with the sulfuric acid can interfere if the particle collection density is large enough. It is felt that the sample times used here are short enough that errors caused by particulate interactions will be well within the limits imposed on the analysis, i.e. ± 20 percent.

The results of measurements for sulfuric acid are presented in Table 31. Sulfuric acid was not detected in the samples collected in February. As indicated in the section concerning the sulfur dioxide data, this could be due to sampling at the edges of the plume where the emitted sulfuric acid is well mixed with the ambient ammonia. On the 18th of January, the sulfuric acid collected with the Micro-Orifice Impactor appears to be neutralized more quickly than that collected with the Cabot dichotomous sampler. Both the Cabot and MOI used a denuder with the same dimensions, but the MOI sampled at twice the flow rate of the Cabot. On the Cabot sampler was used to qualitatively evaluate the denuders. The higher flow rate used with the MOI may have allowed enough penetration of ammonia through the denuders to account for the differences seen in Table 31.

5.2.5 Ammonia Data

Ammonia concentrations are also presented in Table 31. These were obtained by trapping the ambient ammonia on glass fiber filters that had been impregnated with oxalic acid. Particulate ammonium was removed by a prefilter. The filters were extracted into buffer and analyzed for ammonium by the indophenol method.

Table 31. Results of Measurements for Sulfuric Acid Conducted During the Chase Car Experiments in January and February 1979. Values in ( ) are Standard Deviations

		H_2SO_4 (µg/m^3)		$SO_4^=$ (µg/m^3)
Date	Distance Behind Emitter (m)	Cabot	MOI	Cabot
1-10	30	(no sulfuric acid recovered with the manifold at 1.8 m above the road surface)		
1-17	6	79	(manifold inlet moved to 12-18" above surface)	
1-18	15	27(4)	23(2)	52(6)
	29	20(3)	5(1)	43(4)
	59	3(1)	1(1)	11(2)
	88	0	1(0.5)	5(1)
1-25	15	11(4)	12(2)	30(6)
	29	4(3)		13(4)
	44	5(2)		11(3)
	117		0.8(0.7)	
2-27		(no sulfuric acid recovered)		
Ammonia concentration				
1-18	6 ± 2 ppb			
1-25	4 ± 2 ppb			
2-27	6 ± 1.4 ppb			

5.3 DISCUSSION OF THE CHASE CAR EXPERIMENT DATA

5.3.1 Comparison of Sulfate and Sulfur Dioxide Data

Assuming that all of the sulfur emitted from the catalyst equipped car is in the form of sulfate or sulfur dioxide, the fraction of the sulfur converted to sulfate can be given by:

$$f = (\text{S as SO}_4^{=})/((\text{S as SO}_2) + \text{S as SO}_4^{=}))$$

$$f = (\text{SO}_4^{=})k/((\text{SO}_2) + \text{SO}_4^{=})k)$$

where k is the factor to convert ug/m^3 to ppb. The same result can also be obtained by converting the SO_2 concentration from ppb to ug/m^3 as sulfate. The fraction of sulfur converted to sulfate for all the available data is given in Table 32. The overall average conversion is 0.45 ± 0.11.

There is a significant difference in the fractions obtained in January and those obtained in February. Two things could have contributed to this difference:

1. All of the sulfate data in February were obtained using the LBL dichotomous sampler while most of the data in January were obtained with the Cabot dichotomous sampler. The significant dead volume and short sample times used with the Cabot sampler could result in the difference observed.

2. The last set of measurements in January and the set in February were separated by one month. Changes in the catalyst could have occurred over that time period.

These data are plotted in Figure 37 and regression lines are included for sulfate data obtained with the LBL separately from that obtained with the Cabot dichotomous sampler. The values of the slopes are in excellent agreement with the tabulated values indicating consistent SO_2 to $SO_4^{=}$ conversion over the two months these measurements were performed.

The absolute value of this conversion, 40 to 50 percent, is much larger than the 10 ± 4 percent reported by Pierson (1978) for catalyst equipped vehicles during experiments conducted in a tunnel on the Pennsylvania Turnpike. However, it should be remembered that the data reported here were obtained only during

Table 32. Comparison of Sulfate and Sulfur Dioxide Concentrations Measured Behind the Catalyst Equipped Vehicle. Concentrations have been corrected for background. Values in ( ) are estimates of the standard deviations for the listed values.

Date	Time	Distance Behind Emitter (feet) (± 12)	Sulfate ($\mu g/m^3$)	SO_2 (ppb)	Fraction of Sulfur in the form of Sulfate
1/10	1327	100	21.0(1.0)*	7.2(4.9)	0.43(0.17)
1/17	1040	48	79.0(4.0)*	30.3(6.0)	0.40(0.05)
1/18	1552	48	51.0(6.0)*	21.6(5.3)	0.38(0.07)
	1556	96	42.0(4.0)*	14.4(4.8)	0.43(0.09)
	1607	192	10.0(2.0)*	3.3(4.1)	0.44(0.32)
	1616	288	4.0(1.0)*	6.3(4.2)	0.14(0.09)
1/25	1156	48	42.0(8.0)**	18.2(5.1)	0.37(0.10)
	1204	96	23.0(2.0)**	8.4(4.4)	0.41(0.13)
	1215	144	11.0(3.0)*	3.3(4.1)	0.46(0.34)
2/27	1309	48	25.6(0.8)**	6.6(2.3)	0.50(0.09)
	1330	288	11.1(0.4)**	2.6(2.3)	0.52(0.22)
	1335	192	17.3(0.5)**	4.1(2.3)	0.52(0.14)
	1417	96	13.8(0.6)**	6.2(2.3)	0.36(0.09)
	1432	48	40.0(1.0)**	6.5(2.4)	0.61(0.09)
	1527	96	15.5(0.7)**	5.3(2.4)	0.43(0.11)
	1548	48	63.0(1.0)**	11.3(2.5)	0.59(0.05)
	1602	96	21.7(0.6)**	4.1(2.3)	0.57(0.14)
	1614	192	18.5(0.5)**	4.8(2.3)	0.50(0.12)

*Data from Cabot Dichotomous Sampler.
**Data from LBL Dichotomous Sampler.

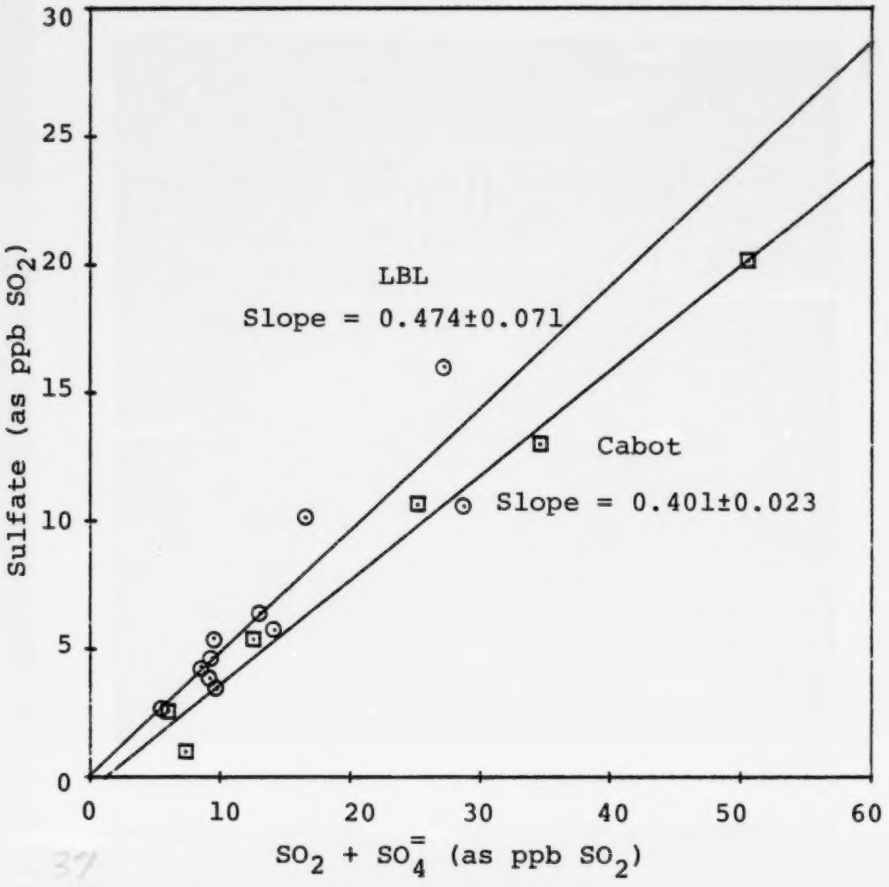

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Figure 37. Sulfate emitted from the catalyst equipped vehicle as a function of the total sulfur emitted (as SO_2). The slopes represent the fraction of the emitted sulfur that is in the form of sulfate.

⊙ - Data from the LBL dichotomous sampler

⊡ - Data from the Cabot dichotomous sampler one brief portion of a driving cycle, and that the strong sulfur dioxide emissions which occurred when accelerating onto the freeway are not included in these results.

5.3.2 The Neutralization of Sulfuric Acid by Ammonia

The data for sulfuric acid concentrations in the vehicle exhaust plume in Table 31 show enough scatter that accurate calculations of the rate of neutralization of the emitted sulfuric acid by the ambient ammonia are not justified. The most complete results were obtained on 18 January 1979, when it was observed that the sulfuric acid was about half neutralized at a distance of 15 m behind the emitting vehicle, and 80 percent or more neutralized at a distance of 88 m. At a driving speed of 55 mph, the reaction times are 0.6 sec and 3.6 sec, repectively. Laboratory studies have shown that sulfuric acid aerosols are rapidly neutralized by ppb concentrations of ammonia (Huntzicker, Ling and Hoffman, 1977) and these data are consistent with those results.

6.0 CONCLUSIONS AND DISCUSSION

6.1 CONCLUSIONS

The following conclusions are primarily based on the experimental results obtained on the Ventura Freeway in October 1978 through February 1979. Measurements were made in heavy traffic during the middle of the day, to avoid the rush-hour slowdowns. Even so, a few measurements were made in variable-speed traffic. The vehicle mix determined by visual counts was about 5 percent gasoline engine trucks, 5 to 10 percent diesels, 35 to 50 percent catalyst-equipped cars, and the remainder non-catalyst cars. Conclusions from the chase-car experiments on the Simi Freeway are also summarized.

1. Sulfate emissions from catalyst equipped vehicles were not great enough to be of concern in Los Angeles in the winter of 1978-1979. This conclusion is based on the following observations:

   A. Values for the in-roadway, fine-particle* sulfate increments on a heavily traveled freeway (the Ventura Freeway) on the days sampled averaged 0.6 ug/m^3, with a standard deviation of approximately 0.6 ug/m^3. This is less than 5 percent of the mean annual sulfate concentration in Los Angeles.

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*Here fine-particle refers to particulates smaller than 3.0 um, and their composition is determined by the analysis of the fine-particle filters from dichotomous samplers. The nuclei mode refers to particles smaller than 0.09 um, and their composition is determined by the analysis of after filters from the Micro-Orifice Impactor.

B. The in-roadway sulfate increment was smaller than the variability of the background sulfate concentrations over a distance of a few miles, except when the sulfate background concentrations were unusually low. Thus, a person's sulfate exposure in Los Angeles usually changes more on traveling a mile or two in the city than it does on entering or leaving the freeway.

C. The in-roadway increment of sulfate in the nuclei mode size range is 0.3 ug/m^3, or about half of the fine-particle sulfate increment. Since the sulfate emissions from catalyst equipped cars were found in this and other studies to be entirely in the nuclei mode size range, less than half the in-roadway, fine particle sulfate increment can be due to catalyst equipped vehicles. The remainder must be due to other types of vehicles, such as diesels.

D. Ambient ammonia concentrations ranged from 2 to 20 ppb during the in-roadway measurements, and averaged 7 ppb. This average ammonia concentration is 24 times the concentration required to neutralize a sulfuric acid concentration equal to the average in-roadway sulfate increment.

E. The in-roadway sulfuric acid concentrations were, with one possible exception, always below the limit of detection (which is about 0.2 ug/m^3), even in the wake of catalyst equipped cars. (The chase car experiments showed that the analytical method is capable of detecting and determining sulfuric acid.)

2. The following observations were made on the analytical methods employed:

A. Replication of the measurements of the fine-particle aerosol showed that the overwhelming majority of the variability in the data for the in-roadway concentration increments was due to real fluctuations in these concentrations rather than due to any lack of precision in the measurement methods.

B. For nuclei mode filter samples collected in the roadway, satisfactory agreement was obtained between X-ray fluorescence (XRF) measurements of sulfur and bromine, and determinations of sulfate and bromide by water extraction followed by ion chromatography.

C. For other samples, the XRF results indicated that the extraction procedures used were less than 100 percent efficient for sulfate and bromide, and that the extraction is less efficient for accumulation mode particles than nuclei mode particles, and also less efficient for samples collected in the background than samples collected in the roadway. Approximate values of the extraction efficiency for fine-particle samples collected in the background are 76 percent for sulfate and 25 percent for bromide.

D. After the above water extractions, the filters were extracted in 10 percent nitric acid, and both extracts analyzed by atomic absorption (AA) for lead. On the average, these AA determinations gave lead values one-half those obtained by XRF.

3. The following observations were made for lead and bromide concentrations.

A. The in-roadway increments in the fine-particle bromine concentration determined by XRF averaged 2.5 ug/m^3, and 63 percent of this was in the nuclei mode size range. The in-roadway bromine concentrations are relatively greater than in the background, compared to other species measured, so the results for the in-roadway increments show greater precision than do those for sulfate or lead.

B. The in-roadway increments in the fine-particle lead concentrations determined by XRF average 5 ug/m^3, and 58 percent of this was in the nuclei mode size range.

4. In-roadway increments in the sulfur dioxide concentration averaged 12 ppb (31 ug/m^3) and the standard deviation associated with the run-to-run variability in the run average sulfur dioxide concentration was between 2 and 3 ppb. The following observations were made for the relations between the observed sulfate, sulfur dioxide, lead and bromide concentrations.

A. The average in-roadway sulfur increment in the form of sulfate was 0.2 ug/m^3 compared to the average in-roadway sulfur increment in sulfur dioxide of 15 ug/m^3. This indicates that between 1 and 2 percent of the fuel sulfur is oxidized to sulfate by the total vehicle population.

B. The ratio of bromine to lead in the in-roadway concentration increments was 0.5, and this result is similar to those from earlier studies, which mostly fall between 0.39 and 0.51. The ratio in Ethyl Corporation TEL Motor Mix is 0.39.

C. Scatter diagrams of simultaneously determined values of the lead and sulfate in-roadway increment show no correlation between the two species in one-hour samples. (Because vehicles using leaded fuel emit little sulfate, a strong anti-correlation would be expected for individual vehicle plumes.) The observed lack of correlation demonstrates the danger associated with surrogate calculations for estimating the concentrations of vehicle-generated pollutants.

D. The bromide to lead ratio is half as great in the background aerosol as in the in-roadway aerosol. This loss of bromide from the aerosol has been frequently observed. No data on the explanation for this were obtained in this study, but it is suggested that a significant contributor to this loss is the reaction of ambient nitric acid with the bromide-containing particulates to form gaseous HBr.

5. The following observations were made when a new, catalyst-equipped compact station wagon traveling on a freeway with very light traffic was followed by one of the instrumented vans. The car burned 0.3 percent sulfur fuel (ten times the California average sulfur concentration), and measurements were made at a constant speed of 55 mph (88 km/hr). The driving cycle included leaving the freeway, turning around, and accelerating to re-enter the freeway at either 7 or 11 mi (11 or 18 km) intervals.

A. Sulfuric acid was easily detected in the exhaust plume, and this acid was rapidly neutralized by ambient ammonia. Concentrations as high as 79 ug/m^3 were observed.

B. The same sulfate concentration increments were observed in the fine-particle samples as in the nuclei mode samples, showing that all the emitted sulfate is in the nuclei size range.

C. Sulfur dioxide and sulfate measurements showed that 35 to 55 percent of the emitted sulfur was in the form of sulfate in the 55 mph (88 km/hr) portion of the driving cycle in which measurements were made.

6.2 DISCUSSION

The in-roadway sulfate increments found on the Los Angeles freeways are considerably smaller than would be predicted on the basis of other studies. Pierson and his co-workers have made measurements in a Pennsylvania Turnpike tunnel, and obtained the results in Table 33 (Pierson, Brachaczek, and McKee, 1979). When those results are converted to the vehicle mix found on the Ventura Freeway, it is estimated that roughly half the in-roadway sulfur dioxide increment is due to diesels and that the fraction of sulfur emitted as sulfate should be in the neighborhood of 4 percent. For the sulfur dioxide increments observed on the Ventura Freeway, this would correspond to average in-roadway sulfate increments of 2 ug/m^3. Increments this large, or larger, were observed in only two sets of samples. When the sulfate increments due to diesel trucks and non-catalyst vehicles on the Ventura Freeway are estimated from Pierson's data, it is found that these emissions alone can account for the observed sulfate increments. At the other extreme, if all the sulfates on the Ventura Freeway were due to catalyst vehicles, and none were due to other traffic, then less than 7 percent of the fuel sulfur in the catalyst vehicles would be emitted as sulfate. However, this extreme can be ruled out because only half the sulfate increment was observed to be in the nuclei mode particle size range.

If the following assumptions are made:

1. The accumulation mode sulfate increment is due to diesel vehicles.
2. One-third of the diesel sulfate is emitted in the nuclei mode size range.
3. Sulfates from other non-catalyst vehicles are neglected.
4. Sulfur dioxide emissions are apportioned among the vehicles according to the observed traffic mix and the emission rate data in Table 33.

Table 33. Sulfate and SO_2 Emission Rates and $SO_2 \rightarrow SO_4^=$ Conversions in the 1977 Tuscarora Tunnel Experiment (Pierson, et al., 1979).

	$SO_4^=$ mg/km	SO_2 mg/km	$SO_2 \rightarrow SO_4^=$ %[a]
All Traffic Average[b]	9.4	214	2.7±0.6
Automobiles (all)	3±1[c]	60±19[c]	3±1
Catalyst	8±3[c]	46±16[c]	10±4
Noncatalyst	0.3±0.1[d]	64±31[c]	0.21[e]
Diesel Trucks	44±5	1055±100	2.7

[a] $SO_4^=$ as mole-% to total emitted sulfur ($SO_2 + SO_4^=$).

[b] Corresponding to overall average traffic composition 84.5% gasoline powered vehicles, 15.5% diesel trucks. 38% of the automobiles were catalyst-equipped.

[c] Highest estimate; obtained by using quartz-fiber filter $SO_4^=$ values and second data analysis method (see reference).

[d] Evaluated from $SO_2 \rightarrow SO_4^=$ in last column (0.21%) and total S consumption figures for noncatalyst gasoline-powered vehicles (see reference).

[e] Adopted from earlier work (see reference).

Then it is estimated that the in-roadway increments due to catalyst vehicles are 0.2 ug/m^3 sulfate and 5.5 ug/m^3 of sulfur dioxide, and the fraction of the fuel sulfur emitted as sulfate by catalyst equipped vehicles is 2.4 percent. This conversion efficiency is similar to that observed for diesel vehicles.

Several factors can lead to lower sulfate emissions on Los Angeles freeways than expected from dynamometer tests or from the Pennsylvania Turnpike data. It is known that variable driving speeds decrease sulfate emissions (Cadle, *et al*., 1976, 1977), and driving speeds are certainly more variable on a heavily-traveled urban freeway than on the Pennsylvania Turnpike. Dynamometer tests are typically performed on vehicles with a controlled history, whereas at least some of the catalyst systems in Los Angeles cars have been abused, for example, by the use of much less expensive leaded fuel.

It is clear from these data that sulfate emissions from catalyst equipped vehicles on freeways in Los Angeles were not a significant problem in the winter of 1978-1979. In the absence of significant changes in exhaust-system control technology, there is no indication that they will become a problem.

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